Environmental Evaluation of the Indirectly Heated Carbonate Looping Process

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EST

Task

The following individual tasks are performed:

-Introduction into carbonate looping process, fluidized bed technology, ASPEN PLUS software and the set-up of the existing plant design.

-Development of a basic steady state Aspen PLUS model according to the existing plant design.

-Development of a mass and energy balance of the overall process

-Investigation of the solid samples (purge) from the test plant regarding composition and particle size distribution

-Evaluation of process data from test campaigns in the 300kWth pilot plant

-Validation of the process model by means of this data

-Evaluation of the sorbent performance by means of a TGA analysis.

Explanaiton

Hiermit versichere ich, die vorliegende _____arbeit ohne Hilfe Dritter nur mit den angegebenen Quellen und Hilfsmitteln angefertigt zu haben. Alle Stellen, die den Quellen entnommen wurden, sind als solche kenntlich gemacht worden. Diese Arbeit hat in gleicher oder ähnlicher Form noch keiner Prüfungsbehörde vorgelegen.

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Content

List of abbreviations

ASU	Air Separation Unit
ACGIH	American Conference of Governmental Industrial Hygienists
BFB	Bubbling Fluidized Bed
CCS	Carbon Capture and Storage
CFB	Circulating Fluidized Bed
FBC	Fluidized Bed Combustion
FORTRAN	Formula Translating System
GHG	Greenhouse gas
IEA	International Energy Agency
IHCL	Indirectly Heated Carbonate Looping
IPPC	Intergovernmental Panel on Climate Change
MDEA	Methyl Diethanolamine
MEA	Monoethanolamine
PEL	Permissible Exposure Limit
PSA	Pressure Swing Adsorption
TGA	Thermogravimetric Analysis
TLV	Threshold Limit Value
TSA	Temperature Swing Adsorption
TWA	Time Weighted Average

List of symbols

Latin characters

A	Area	m^2
C	Concentration	g/mol
d	Diameter	m
g	Acceleration of gravity	9.81 m/s^2
g_c	Conversion factor necessary to have a consistent system of units	1kg m/s^2 N
h	Specific enthalpy	J/kg
K_S	Kinetic constant	m^4/mol·s
M	Molar mass	g/mol
m	Mass	kg
N	Number of carbonation/calcination cycles	cycles
n	Number of moles	mol
P	Pressure	Pa
p_i	Partial pressure of the gas i	Pa
Q	Heat transferred	J/kg
q	Solids mass flow	kg/s
R	Gas constant	8.3144621 J/mol·K
r	Change solid mass due to heterogeneous chemical reactions	kg/s
T	Temperature	°C
u	Velocity	m/s
V	Volume	m^3
v	Rate of reaction	m/s
W	Exchange work	J/kg
X	Carbonation conversion	[-]
z	Height	m

Greek characters

ρ	Density	kg/m^3
Δp	Pressure drop	$Pa(N/m^2)$
ε	Void fraction	-
ψ	Sphericity	-
μ	Viscosity of a Newtonian fluid	kg/m·s

Indices

ave	Average
mf	Minimum fluidization
g	Gas
s	Solid
p	Particles
t	Transversal
o	Surface area
in	Inlet
out	Outlet
vc	Volume of control

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1. Introduction

1.1 Motivation

It seems, that the world's population is every time becoming more aware in adding to the world's protection of greenhouse gases that contribute to global warming and ensuing climate change. In the last years has been a considerably progress in scientific research and knowledge on climate change in which every time more, human activities and burning fossil fuels win more weight as a reason for the current warming of the Earth's climate. Increasingly, the target of reduction of GHG is getting stronger. The Kyoto Protocol shares the objective to stabilize atmospheric concentrations of GHGs a level that will prevent dangerous interference with the climate system. Between the period 2008-2012 its target was to cut the GHG back in nearly 5% compared to 1990.[1] In September 2007, industrialized signatory countries of the Protocol of Kyoto agreed, in a meeting of the United Nations in Wien, the necessity of cut back the GHG between de 25% and 40%. The EU, its 28 Member States and Iceland have inscribed a commitment of reducing average annual emissions by 20% during the 2013-2030 period, as compared to base year (1990).[2]

1.2 Future of coal

Coal is the most abundant fossil fuel used for the electric power generation as well as the largest worldwide source of CO_2 emissions contributing in this way to the greenhouse effect and global warming. Its global demand increased between 1990-2011 60% according to the International Energy Agency IEA. [3]

Coal is for Europe a vital source of energy. With around 750 million tons of coal equivalent is Europe -including Russia-, the third largest consuming region in the world after China and North America. The largest consumer of coal in the EU is Germany, followed by Poland. Especially for the safe and competitive electricity generation in the EU, coal plays a central role. More than a quarter of the total EU electricity comes from coal.[4]

Coal plays a decisive role on electricity in Germany, Europe and worldwide, and several studies conclude that together with gas will play an important role in the future energy of the EU. At least 10GW of additional coal power capacity is planned or under construction in Europe.

Coal is necessary to cover the energy's world demand and it will remain one of the main sources of primary energy. In prognostic until the 2030 energy consumption will increase specially due to the growing economies lead by China and India. Furthermore the future energy policies will be based on the growing energy demands on developing countries and in the need of a significant reduction in greenhouse gas (GHG) emissions. [5]

Nevertheless, EU's intention to decarbonize coal economy cannot be neglected. For this reason, coal and other fossil fuels will have to be decarbonized over the coming years. Therefore it is crucial the development and deployment of CCS technologies. Many EU Member States take into account to include a change in technology of fundamentally new system technology, a change in fuel use and additionally flue gas cleaning technologies.

The forward-looking decisions of European energy policy play a central role in the future structure of the European electricity generation. The EU's dependence on rising oil and gas imports also need an answer to the orientation of technology policy and promoting low-emission energy technologies. With the European trading system for CO_2 emission, efforts to reduce CO_2 emissions have clearly shifted to the energy industry. [6]

The European coal industry has had therefore prepared a comprehensive report on the future role of coal in Europe. In this report are analyzed different scenarios and all scenarios get to the results that in 2030 energy will be still based in the use of fuel energy and because the price and supply safety all energy will be necessary. Also decisive for the future role inside the European electricity will be the development of the price gap between gas and coal.

Separately analyzing each country according to IEA studies; In China Coal is dominating the market and India is the world's third largest coal consumer and demand for the fuel is foreseen to grow in coming decades. Australia is the world's second-largest coal exporter and the US uses the most coal of any developed economy, according to the IEA and even the well country's publicized shale gas boom, coal is still the main fuel used for electricity generation (40% of US's power in 2013, gas producing 29%). In the EU the European commission expect to lower until the half the energy consumption from coal by 2050 (from 16% to 8%). Furthermore renewables will take an important role in electricity generation for what less coal is expected to be used. [3]

The European Council confirmed that the EU's aim is the reduction of Greenhouse Gas emissions of 80-95% by 2050 compared to 1990. A mechanism that could help is CCS –Carbon capture and storage-. CCS is a mechanism where carbon is separated from coal and injected underground for long term storage. It might be used to mitigate the coal's industry's greenhouse gas emissions but it is still facing some problems, being the cost the initial problem and the social acceptance has still to be worked. CCS may be a solution for fossil fuel emissions but it's also relevant for industrial installations with a significant share of chemically determined process emissions.

2 Theoretical Fundamentals

2.1 Current technology

2.1.1 Overview of CO_2 capture systems CCS

Carbon Capture and Storage (CCS) is refered to these technologyes developed to capture carbon dioxide that would otherwise be emitted to the atmosphere and injected it in deep geological formation to be stored. The main application of CCS is in fossil fuel power plants and in other industrial plants (i.e, steel manufacturing, cement manufacturing).

In the next figure are exposed the main routes to CO_2 capture for industrial applications and power plants. This three systems for capturing CO_2 from use of fossil fuels and/or biomass are explained in this section.

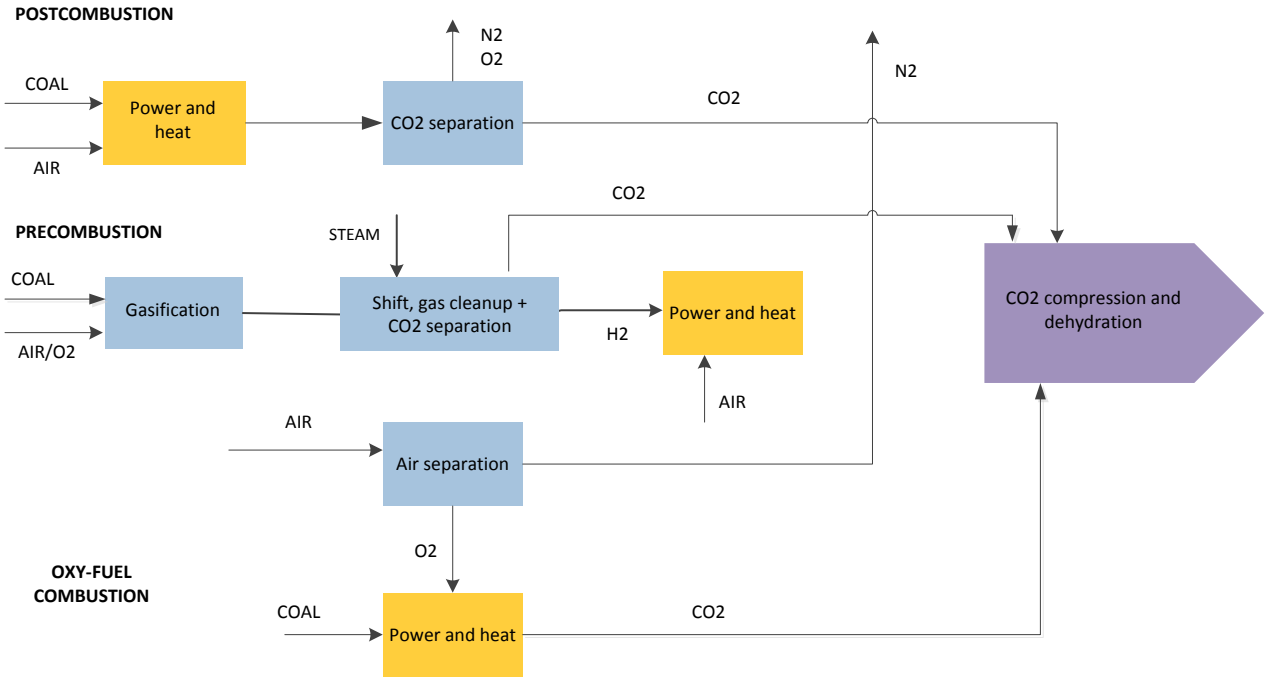

Figure: 1 CCS systems – Data extracted from [7]

2.1.1.1 Post combustion

Post combustion is the process that captures CO_2 from flue gases produced by combustion of fossil fuels and biomass in air. Before discharging the flue gas to the atmosphere most of CO_2 is separated. Then the CO_2 is directed to a storage reservoir and the remaining flue gas is released to the atmosphere. In large scale processes such as power plants, furnaces in industries, cements kilns and steel production plants this process has been economically the best technology to use the fuel energy.[8]

As normally, post combustion capture systems can be applied to the flue gases produced to the combustion of any type of fuel, taking always into account the impurities on the fuel, which are very important for the design and cost of the plant. Depending on the type of fuel used the CO_2 concentration can vary in a wide range (between 3% in natural gas combined cycle to 15% for a coal fired combustion plant). Also, coal combustion will not only contain CO_2, N_2,O_2 and H_2O in its flue gas but also other pollutants such as SO_x, NO_x, HCl, mercury, other metals and trace organic and inorganic contaminants. This system can be integrated as a retrofit or directly added to an existing power plant.

There are a lot of commercially process technologies which can be used for capture of CO_2, however, comparative assessment studies (Hendriks, 1994; Riemer and Ormerod, 1995; IEA GHG, 2000b) according to IPPC Report [8] have shown that the most viable processes for post combustion CO_2 capture are calcination-carbonation cycle and chemical absorption based on chemical solvents. They offer high capture efficiency. Other options are less used either for its low development or its high cost. Among these are included physical adsorption, cryogenic distillation and membranes. [9] About the processes for post combustion CO_2 capture; Calcination and carbonation cycle is explained with more detail throughout this work. In this section a brief description of the others processes is performed.

Chemical absorption: The most widely used CO_2 capture technology for chemical and natural gas industries is the chemical absorption process using amines. The fundamental underlying principle is the exothermic, reversible reaction between a weak acid (e.g., CO_2) and a weak base (e.g., MEA) to form a soluble salt.

Physical adsorption: Basically it is responsible to use materials capable of adsorbing CO_2 at generally high temperatures, and then recover it by processes of change in temperature or pressure (TSA and PSA processes respectively).

Membranes: This process is used in the capture of CO_2 from natural gas at high concentrations of CO_2 and at high pressure; otherwise (low pressure) force driving for gas separation required is very low. This system entails higher energy penalties compared with chemical absorption, and also incurs a smaller percentage of CO_2 removal. The main drawback of this process is the low permeability with respect to CO_2.

Cryogenic distillation: It consists in a series of stages of compression, cooling and expansion, in which the gas components can be separated in a distillation column. This technology is primarily used to remove impurities from a stream of high purity CO_2. As backward even the high purity liquid CO_2 produced ready for sequestration, the extremely energy of the process makes it ineffective. [10]

2.1.1.2 Oxy-fuel combustion

Oxy-fuel combustion burns fuel in pure oxygen instead of air as the primary oxidant. An air separation unit (ASU) removes nitrogen from the air producing oxygen. In this process fuel consumption is reduced because nitrogen component doesn't take part in this process. The oxygen is injected with the fuel into the boiler where combustion takes place. If fuel is burnt in pure oxygen, the flame temperature becomes high, but CO_2 and H_2O-rich flue gas can be recycled to the combustor to moderate this effect. The captured CO_2 is ready to be compressed and dehydrated for transport and storage.

There is currently research being done in firing fossil-fueled power plants with an oxygen-enriched gas mix instead of air. Almost all of the nitrogen is removed from input air, yielding a stream that is approximately 95% oxygen. Oxy-fuel combustion produces exhaust mainly compound with CO_2 and H_2O. After the water vapor is removed (cooling and compressing) it produces flue gas rich of CO_2. It is necessary to remove the water vapor in order to prevent condensation and corrosion in pipelines. The net flue gas, after cooling to condense water vapor, contains from about 80%-98% CO_2 depending on the fuel used and the particular oxy-fuel combustion process. The impurities found in the flue gas derive from the fuel used and the inert gas components. [11] This system has yet to be deployed on a commercial scale.

2.1.1.3 Pre combustion

In a pre-combustion, the carbon content of the fuel is reduced prior to combustion, so after combustion, a stream of pure CO_2 is produced.

As a first step, a fuel reacts with oxygen or air and/or steam to give mainly a synthesis gas composed of carbon monoxide and hydrogen. If the process is done adding steam the process is called steam reforming, and if it's done adding oxygen the process often is called partial oxidation. Moreover, if what is used as a fuel is natural gas, the syngas is produced by steam reforming. If coal is used as the fuel, it is obtained by gasification.[12]

The next step is converting CO to CO_2 by the addition of steam. The products obtained are CO_2 and H_2.

Finally, the last step is the separation of CO_2 that's removed from the CO_2/H_2 mixture. The result is in a hydrogen-rich fuel which can be used in many applications –boilers, furnaces, gas turbines, engines and fuel cells- and CO_2 available for storage.

The system is closer related to the production of hydrogen, which is an important agent in different processes such as: The synthesis of ammonia, fertilizer production and the hydro processing oil refineries.

Pre-combustion capture can be used mainly for two applications:

The first one, as already mentioned above, is to produce hydrogen being carbon free. And secondly, the process can reduce the carbon content of fuels with the excess carbon, which usually is removed as CO_2.

The following processes are the most commons in pre-combustion: Cryogenic separation, chemical and physical absorption and membrane separation.

Cryogenic separation physically separates CO_2 condensing syngas at cryogenic temperatures. When the system used is with chemical absorption the process is usually called amine scrubbing being this one the most used CO_2 removal technology. Amine scrubbing uses a solution with Methyl diethanolamine (MDEA). Moreover, physical absorption is suitable for CO_2 high partial pressures. And finally the membrane separation still needs development to be used at large scale, but is commercially useful for separate hydrogen. [12]

2.1.2 Fluidized bed reactors

Fluidized bed reactors (FBR) are chambers that allow the mixing of fluid substrates with powdered catalyst in which the mass of catalyst fluidizes performing effective mixing and highly efficient transport processes. FBR are very important to chemical engineering due to its excellent heat and mass transfer characteristics.[13] The main characteristic of fluidized bed reactors is that frictional forces between particle and fluid counterbalance the weight of the particle achieving the bed of inert material to be suspended by a flow of air or gas.

They are called multiphase reactors when they are dealing with more than one phase in it. The carbonate looping process is based on fluidized bed reactors because of its good mixing and large contact area between phases and also enhances chemical reactions, heat transfer and mass transfer.

In this work it is going to focus with gas-solid fluidized bed reactors. In these reactors, a gas is the continuous phase and solid particles are suspended within this continuous phase. The reactor contains a dense bed of fluidized solid particles. Further increase in gas flow rate decreases the bed density. [14] Also reactor configuration, its properties (angularity, surface roughness), and solid flux are important parameters for the quality of

fluidization. Grace [15] The features and behavior of a fluidized bed are highly depend on the material fluidized – usually a solid- and the fluidizing medium –a fluid- properties.

There exist three types of fluidized bed reactors: bubbling fluid reactor, circulating fluid reactor and transport reactor. The differences between these reactors mainly lie in the powder catalyst settling rates and in the location of the gas input. In the bubbling fluid bed reactor the powder catalyst rate is balanced with the velocity of the fluidizing gas going upward. In this reactor the gas input is located at the bottom of it. The circulating fluidized bed differs in that the powder catalyst settling rate is higher than the velocity of the input gas. Furthermore the gas input is located on the side. As last reactor, in transport reactor the containing powder catalyst settling rate is lower than the velocity of the fluidizing gas.

A main parameter to define in a fluidized bed is the minimum fluidization velocity. This one is the gas velocity at which fluidization begins. If gas velocity increases beyond this minimum velocity, the bed will expand and depending on the size solids particles, bubbling regime might starts -for large solids-. When the gas flow rate increases slugging may occur. In slugging state the bubbles grow in size, coalesce and they cover basically the entire bed.[16][13] This is an undesirable state due to it causes erratic pressure shocks and poor gas/particles contact. Raising the flue gas even further pneumatic transportation regime is achieved, where solid particles convey out of the vessel. Furthermore with further increase of gas velocity the entrainment between solids become very high so that gas-solid separators become necessary. Using bed expansions and higher flow rates gives higher mass transfer rates from the fluid to the particles. Furthermore obstructions and dead zones will be also avoided. The requirements of fluidization flow rate rarely coincide with the efficiency for complete conversion, then recycling is necessary to obtain good fluidization.[13] In the next illustration a schematic of different fluidized bed regimes is shown.

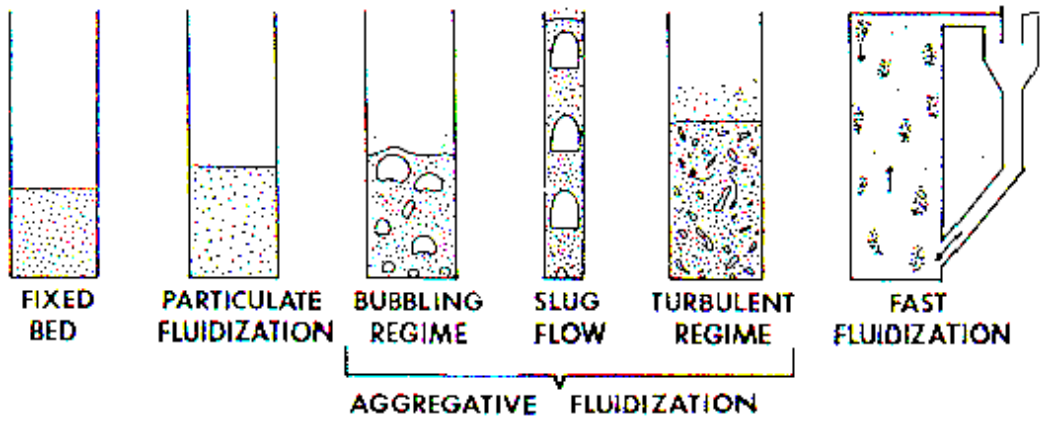

Figure: 2 Fluidized bed regimes – from Fluidized bed reactors [13]

The main advantages are that they are compact, simple in construction and easily scalable, they has high thermal efficiency and ease of process control due to stable conditions. Contrary, as disadvantages, they don't

have uniform flow patterns thus complicating their prediction also, the agglomeration of particles decrease the effective surface and the walls of the bed experiment erosion. [17] Fluidized bed reactor are used in a wide range of applications in various industrial operations, inter alia chemical, mechanical, petroleum, mineral and pharmaceutical industries. In this work is not going to enter into detail about the hydrodynamics of FBR, but they are very important and must be well understand for a proper choice of operating parameters for the appropriate fluidization regime. [14]

Solid mass balance in a reactor:

The overall solid mass balance in the reactor follows the equation form:

$$\frac{dm_s}{dt} = \sum q_{s,in} - \sum q_{s,out} + \sum r_s \qquad \text{Equation 2.1}$$

Where m_s is the total mass bed of the reactor [kg], $q_{s,in}$ and $q_{s,out}$ represents the terms of solid mass flow in and out [kg/s] respectively. Finally the sum of r_s represents the total change in solid mass because of heterogeneous chemical reactions [kg/s].

Gas mass balance of a control volume, i

$$\frac{dm_{g,i}}{dt} = \sum q_{g,in,i} - \sum q_{g,out,i} + \sum r_{g,i} \qquad \text{Equation 2.2}$$

Where m_g describes the total gas mass in the domain [kg], and $q_{g,in}$ $q_{g,out}$ the gas flow in and out respectively [kg/s]. $r_{g,i}$ represents the combined effect of the chemical reactions on the gas balance -carbonation, calcination, sulfation, combustion of char and volatiles-.

Moreover , according to Levenspiel [18] the frictional loss required in fluidized bed reactors is cited as follows:

(Frictional force exerted by the fluid on the particles) = (Net weight of solids in the bed)

$$\Delta p_{fr} \cdot A_t = A_t \cdot L_{mf}(1 - \varepsilon_{mf})(|\rho_s - \rho_g|)\left(\frac{g}{gc}\right) \qquad \text{Equation 2.3}$$

$$\left(\begin{array}{c}\text{Frictional}\\ \text{pressure drop}\end{array}\right)\left(\begin{array}{c}\text{Transversal}\\ \text{area of fluidized}\end{array}\right) = \left(\begin{array}{c}\text{Bed}\\ \text{volume}\end{array}\right)\left(\begin{array}{c}\text{Solid}\\ \text{friction}\end{array}\right)\left(\begin{array}{c}\text{Specific net}\\ \text{weight solids}\end{array}\right)$$

2.1.3 Minimum fluidization velocity

Fluidization is known as a process where the granular material changes its static solid state to a dynamic fluid state. This process is achieved when a fluid passes up through the granular material.[19] To achieve the dynamic state is necessary that the fluid introduced through the bottom of the reactor achieves a minimum velocity. With low gas velocities the bed remains in a fixed state. When the velocity increases, the aerodynamic drag forces start to counteract the gravitational forces originating a volume expansion of the bed due to the particles move away from each other. When a fluid passes upwards through a bed of particles the pressure loss in the fluid due to frictional resistance increases with increasing fluid flow. [17] Fluidization finally occurs when the velocity is enough to suspend the solid particles in the upward flowing stream of fluid. The minimum velocity at which this pressure drop over the bed is balanced with the particles weight per unit surface is called minimum fluidization velocity.

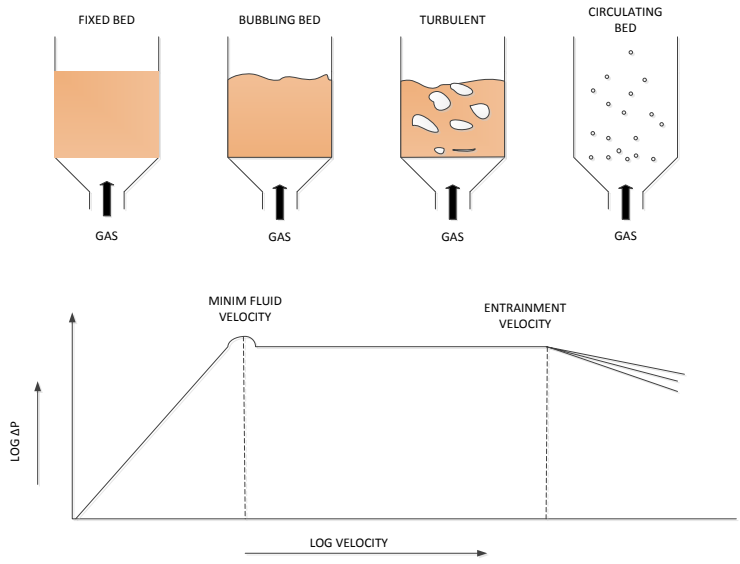

Figure: 3 Fluidized Bed regimes

According to a bed model from Kunii-Levesnpiel ,1969 , the minimum fluidization velocity U_{mf} can be calculated according equation 2.4.

$$U_{mf} = \frac{(\Psi \cdot d_p)^2}{150 \cdot \mu}[g(\rho_s - \rho_g)]\frac{\varepsilon_{mf}^3}{1-\varepsilon_{mf}} \qquad \text{Equation 2.4}$$

To a correct understanding of this equation some variables first need to be introduced.

Ψ known as sphericity is a dimensionless parameter. It is a measure of a particle's no ideality in both shape and roughness.

ε_{mf} is also a dimensionless parameter and is the void fraction at the point of minimum fluidization.

Where the volume of spherical particle V_p , sphericity and the void fraction at the point of minimum fluidization can be calculate according these equations: [20]

$$V_p = \frac{\pi d_p^3}{6} \qquad \text{Equation 2.5}$$

$$\Psi = \frac{Ao}{Ap} = \frac{(\pi\left(\frac{6V_p}{\pi}\right)^{\frac{2}{3}})}{Ap} \qquad \text{Equation 2.6}$$

A correlation used according Wen and Yu,1996 is:

$$\varepsilon_{mf} = (\frac{0.071}{\Psi})^{1/3} \qquad \text{Equation 2.7}$$

2.1.4 Fluidized Bed Combustion

In1970s and 1980s the development of fluidized bed combustor was boosted for the necessity for energy technologies with low emissions of NOx and SOx. [10]

FBC is a combustion technology which allows greater fuel flexibility in addition to a better use of the fuel and better heat transfer. It is principally known for its ability to burn low-grade fuels with low calorific value, high ash content and high moisture content. More advantages are the emission performance and the possibility to be implemented in an existing plant.

Two main variants have been developed from the initial one as the technology has been evolved:

Bubbling Fluidized Bed: characterized by the ability to deal with difficult ignition fuels such as high moistures fuels, high ash fuels and low volatile fuels.

Circulating fluidized bed: known to be best in terms of sulfur removal and in efficiency.

The design of the FBC mainly depends on the fuel and the required steam conditions. Moreover its installation is subjected to the emissions requirements. There are some noticeable differences between the two variants of FBC regarding design parameters;

Table: 1 Extracted from Development of fluidized bed combustion Joris Koornneef [21]

Design parameters	BFB	CFB
Combustion temperature(°C)	760-780	800-900
Fuel particle size(mm)	0-50	0-25
Fluidization velocities (m/s)	1-3	3-10
Particle concentration	High in bottom, low in freeboard	Gradually decreasing along furnace high

BFB is less sensitive to variations in the fuel moisture content being suitable for biomass and waste firing. It is also characterized by its low fluidization velocity and high residence time of bed material. For these reasons, allows larger fuel particles and with lower calorific values.

In CFB the fluidization velocity is higher. It results in that the solids are entrained in the air flow more equally along the combustor height. The heat transfer and particle concentration gradually decreases along with combustor height. Also the combustion temperature in BFB is usually lower because of the poor fuel quality and its conditions.

Before feeding the fuel into the reactor a first preparation has to be carried out (sizing and drying of the fuel and separation of non-combustibles from the fuel). The fuel can be injected into the reactor only once the velocity is high enough to achieve the flow to suspend the particles in the bed. [21] The zone above combustion zone is called freeboard where the density of solid particles is low. In the bottom of the furnace there is bed material. The air supply lifts the bed material and coal particles keeping them in suspension. There is where combustion takes place. The air nozzles at the bottom of the bed allows air flow without clogging.[22] The particles are carried with the flue gas upward and then enter into a cyclone where the heavier particles separate from the gas.

The combustion efficiency known as the ability of a furnace to burn carbon is usually higher for CFB than for BFB, because of the better mixing and smaller particles. Regarding to emissions; the emissions of SO_2 are very low for FBC. This can be achieved by injecting limestone into the furnace. This sorbent react with the sulfur

producing a solid named gypsum. Because of the relative low temperature of FBC (BFB and CFB) there is very low NOx formation. Contrary, low combustion temperatures enhance the formation of N_2O (nitrous oxide). Regarding the scale up, FBC are available in a wide range. The biggest units under construction are 550MWe Benson supercritical CFBs for coal in Korea. CFB has the highest maximum capacity 520MWe. BFB version has 142MWe.

2.2 Thermodynamic Fundamentals

2.2.1 First law of thermodynamics

The first law of thermodynamics also known as a principle of conservation of energy states that if performs work or it exchanges heat with another, the internal energy of the system changes.
For analysis of systems whose borders allow the exchange of matter around is convenient to consider a control volume (vc). Energy is transferred by heat, work or accompanying materials into or out. The energy balance for a control volume is given by:

$$\frac{dE_{vc}}{dt} = Q_{vc} - W_{vc} + m_{in}\left(h_{in} + \frac{1}{2}U_{in}^2 + gz_{in}\right) - m_{out}\left(h_{out} + \frac{1}{2}U_{out}^2 + gz_{out}\right) \quad \text{Equation 2.8}$$

The rate of energy within a control volume equals the difference between the rates of energy input and output thereof. [23] In this work both kinetic energy and potential energy can be despised because if compared with the supplied heat, power and enthalpy in the area are very small.

2.2.2 Ideal gas law

To describe the behavior of pressure, temperature and volume of gases is in most cases enough for non-critical or near-critical conditions, the thermal equation of ideal state:

$$PV = nRT \quad \text{Equation 2.9}$$

Where *R* is the gas constant with a value of 8.3144621 J/mol·K and *n* the number of moles
The specific volume and the density are clear proportional to the pressure behavior.

The ideal gas equation is a good approximation for temperatures below the critical temperature and pressures under supercritical pressure. For gas mixtures, the density is about the density of the individual gases and their partial pressures calculated according to equation 2.10.

$$\rho_g = \sum \frac{p_i}{R_i T} \qquad \text{Equation 2.10}$$

2.2.3 Principle of conservation of mass

The principle of conservation of mass for a control volume is expressed as follows: the rate of accumulation of material within the control volume at time t is equal to the difference between the instantaneous mass flow rates into and out of volume control at time t:

$$\frac{dm_{vc}}{dt} = m_{in} - m_{out} \qquad \text{Equation 2.11}$$

2.3 Carbonate looping process

The principle of the carbonate looping process is based on the reversible equation 2.12.

$$CaO_{(s)} + CO_{2(g)} \Leftrightarrow CaCO_{3\,(s)} \quad \Delta H_r = -178 \frac{kJ}{mol} CaCO_3 \qquad \text{Equation 2.12}$$

It consists in capturing CO2 from the flue gas in the carbonator reactor at around 650°C. The calcium oxide reacts with the flue gas, forming $CaCO_3$ and CO_2 depleted flue gas, which leaves the reactor. In a second reactor $CaCO_3$ is calcined at around 950°C regenerating back calcium oxide and CO_2 is released. To establish a closed loop, the regenerated calcium oxide is directed back to the carbonator.
The general layout in the carbonate looping is presented in the next figure.

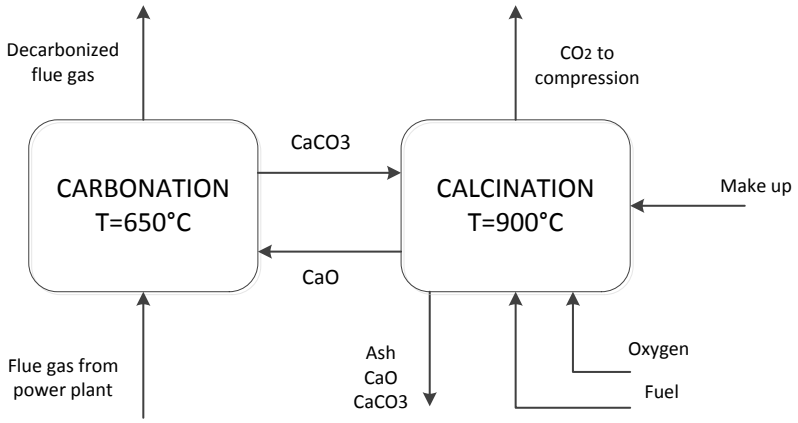

Figure: 4 Carbonate looping scheme

The process is explained with more detail below:

Carbonation of CaO to $CaCO_3$

The first step consists in a flue gas entering into the reactor which is filled with CaO. The flue gas entering the carbonator is originated from a previous combustion of fuel with air in a conventional power plant. The reactor temperature is approximately 650°C. Most of CO2 contained by the flue gas is absorbed by CaO and converted to $CaCO_3$. Almost all SO_2 reacts with CaO too, forming gypsum $CaSO_4$. Due to the exothermic reaction that's carried out, the temperature tends to increase. For this reason, the reactor is provided with launches in the inside to cool it when necessary.

Calcination of limestone

In the calciner, a second reactor is where calcination takes place. The $CaCO_3$ coming from the carbonator is calcined at a high temperature giving rise to a regenerated CaO and a highly concentered CO_2 gas flow which can be compressed and transported to a storage site. The regenerated CaO is returned to the carbonator where it resumes capturing CO_2 from the flue gases.

To reach the calcination step is necessary to heat the reactor up to 800°C. Heat is required to maintain the reaction due to the endothermic CO_2 release. The temperature for the calciner can be achieved by means of a directly heated with fuel and air/oxygen or from external heat sources.

It's a high temperature process, and so high grade-excess heat provides the distinctive characteristic of this capture system. With this process is possible to generate additional power from the various high-temperature sources in the capture system, thus reducing the overall efficiency penalty of the process.

2.3.1 Different configurations of the carbonate looping process

Different models have been designed according to the way of heating the calciner due to its necessity to be supplied with heat because of the endothermic reaction that takes place inside it.

There are two different ways to provide heat to the calciner; Direct or indirectly heated carbonate looping process.

Directly heated carbonate looping: In this configuration the calciner is directly heated by addition of fuel and oxygen. The need of air falls in the necessary implementation of an ASU (Air Separation Unit). The efficiency penalty in this system is mainly caused by the energy demand of the oxy-fuel combustion. The ASU implies a fall of the efficiency.

Indirectly heated carbonate looping: The aim of the indirectly heated calciner is to heat up the incoming sorbent, which consist of $CaCO_3$ and CaO, and to calcine the incoming $CaCO_3$. The heat for calcination reaction is supplied by a circulating fluidized bed combustor. The heat pipes are heated by means of a fluidized bed heat exchanger that is placed next to the calciner.

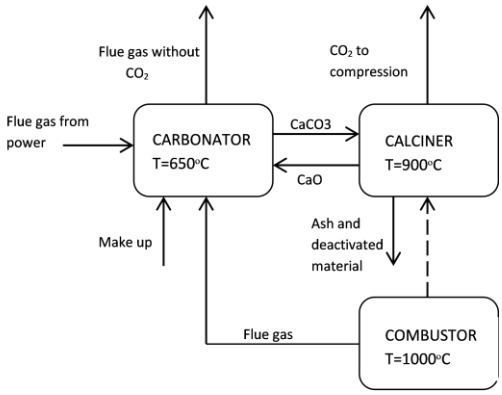

Figure: 5 Indirectly Heated Carbonate Looping Process

When it's about a retrofit configuration of the indirectly heated carbonate looping process –Figure 5-, the gas stream from the combustor is directed to the carbonator what provokes high energy requirements compared to the standard plant.

The main advantage of this process is the avoidance of oxygen production by Air Separation Unit, which leads to an increase of efficiency compared with the standard configuration. Furthermore when coal-fired, the sorbent is kept pure of sulfur, iron and other elements for the simple fact of don't being heating directly into the calciner.

The indirectly heated carbonate looping, newly built plant: This configuration is no longer a retrofit from a coal-fired power plant, but the construction of a new power plant with the carbonate looping system integrat-

ed in it. It undergoes a decrease of the calciner heat consumption because of the less circulating solid mass flow in the system. According to a study from the TU Darmstadt, this option is probably the best solution since less thermal power is needed and higher CO_2 capture rates can be achieved compared to the retrofit options.

There exist different retrofit configuration of the indirectly heated carbonate looping process. A brief overview is going to be carried out in the following lines.

Indirected heated carbonate looping process with solids preheating: One possible configuration is with a heat exchange; preheating the solids directed to the reactors. The solid stream coming from carbonator (650ºC) can be preheated by the hot CaO stream (900ºC) from the calciner, e.g. by means of heat pipes, before to entering the calciner. This action could lower the energy demand of the calciner and thus the corresponding plant size.

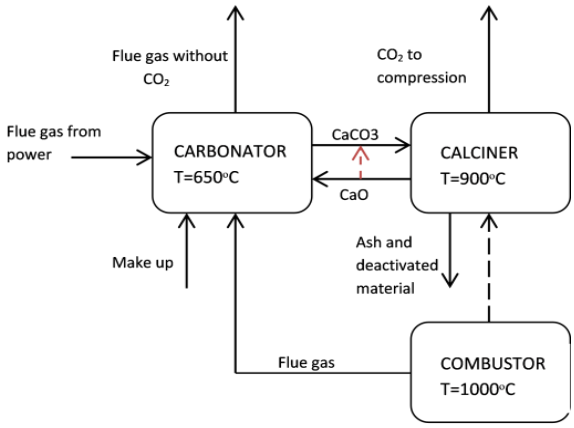

Figure: 6 IHCL Solids preheating

Another configuration classification can deal with the parameters regarding the combustor.
Oxy-fuel fired indirectly heated carbonate looping retrofit configuration: One different configuration can be to feed the external combustor with oxygen instead of air. In this case the flue gas of the combustor will be mainly composed of CO_2 and H_2O and after removing the water vapor this flue gas can be mixed with the CO_2 removed from the power plant. The advantage of this configuration is the reduction of energy required in the calciner because no inert components are mixed with the sorbent. Thus, the thermal power is also low because no inert ash is present in the system.
Biomass-fired retrofit for the indirectly heated carbonate looping process: Another option can be to consider biomass as fuel for the combustor. As advantage the flue gas from the combustor can be directed to a stack and doesn't need to be transferred to the carbonator.[24]

2.3.2 Carbonation calcination equilibrium

Limestone decomposition is a gas-solid reaction in which the solid is the reactant. The reaction involves mass- and heat-transfer processes between a solid limestone particle and the calcination gas. [20] Silaban et al. (1996) and Shimizu et al. (1999) proposed the use of calcium-based sorbents to capture CO_2 from gases at high temperatures based on the reversibility of the reaction:

$$CaO_{(s)} + CO_{2(g)} \Leftrightarrow CaCO_{3\,(s)} \quad \Delta H_r = -178\frac{kJ}{mol}CaCO_3 \qquad \text{Equation 2.12}$$

Carbonation is known as the formation of limestone from calcium oxide and carbon dioxide and calcination as the decomposition of $CaCO_3$ to CaO and CO_2 being subjected to the following reversible reaction. The equilibrium between the carbonation and calcination reaction is described by Baker in 1962, who developed an expression to describe the equilibrium. [13]

$$P_{eq} = 4{,}137 \cdot 10^7 e^{\left(\frac{-20474}{T}\right)} \qquad \text{Equation 2.13}$$

In the following graph is described the equilibrium curve of limestone decomposition [Baker, 1962]

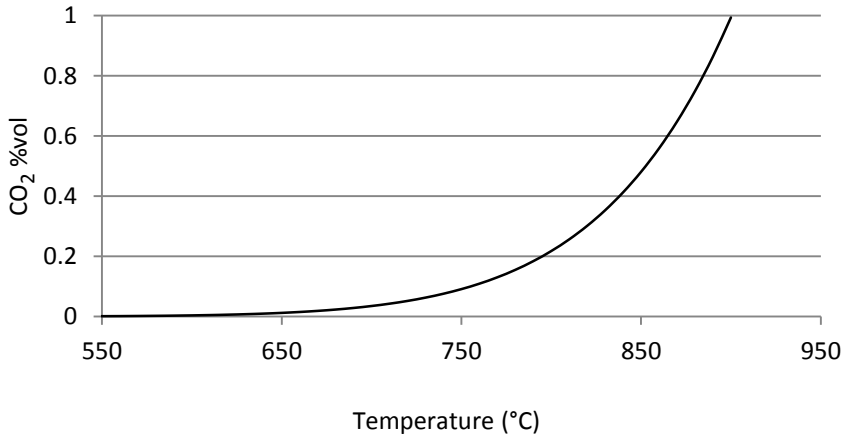

Figure: 7 CO_2 equilibrium, Baker 1962

The carbonation reaction is exothermic and the backward step, known as the calcination reaction, is endothermic. Partial pressure of CO_2 greater than the equilibrium partial pressure at a given temperature will favor carbonation –Figure 7 -. The carbonator temperature is chosen as a compromise between the higher equilib-

rium –maximum- capture at lower temperatures and a decreased rate of reaction, i.e. between the reaction equilibrium and reaction kinetics.

The operation temperature if chosen at 650°C implies around 1,2%vol CO_2 theoretically to be achievable by capture in the flue gases.

In calcination the equilibrium pressure of CO_2 at 1 atmosphere occurs above 850°C, for that reason the process of calcination must be carried out above this temperature. Because of the endothermic reaction, this will be favored by higher temperatures. The proper calciner temperature is chosen as a compromise between higher temperatures, which increase the rate of calcination and milder temperatures which protect the sorbent.[25]

The temperature and pressure of the carbonator establish an upper limit of CO_2 capture efficiency because of the equilibrium of the carbonation reaction. The higher the CO_2 concentration is, the temperature increases and higher the rate reaction will be. It means due to the following reaction -equation 2.14- that higher rate reaction implies a higher CO_2 concentration.

$$\frac{dX}{dt} = k_s S_N (1-X)^{\frac{2}{3}} (C_{CO_2} - C_{CO_2,eq}) \qquad \text{Equation 2.14}$$

Equation 2.14 describes the first order carbonation rate. K_S represents the kinetic constants ($m^4/mol \cdot s$), X the CaO conversion, C_{CO2} the CO2 bulk concentration (mol/m^3) and $C_{CO2,eq}$ the CO_2 concentration in equilibrium (mol/m^3). S_N represents the surface area available for reaction in a particle cycled N times. [26]

There's a great advantage of using Ca-sorbent which works with high temperatures -from 650°c-. In this case, the energy used for calcination is recovered in the carbonator at temperatures still sufficiently high. Contrary, in low temperatures this heat delivered for calcination is not efficiently recovered in steam cycle.[27]

2.3.3 Deactivation of sorbent

CaO as sorbent is very promising in many aspects compared with other sorbents. It has many advantages such as low cost and a higher capacity to absorb than any other sorbent was used. Theoretically sorbent would continually react 1 mol of CO_2 per mol CaO each cycle. By chemical reaction CO_2 is linked to the particles surface of the sorbent forming a limestone layer. The reaction then continues more slowly because the CO_2 has first to diffuse under this layer to come into contact with lime and the pores of the lime particles sinter. Then a transition in the carbonation reaction from a fast to a slow rate prevents the full conversion to $CaCO_3$ on a timescale useful for industrial purposes. Lysikov et al. [28] presented a simple schematic diagram of the behav-

ior of a limestone- sorbent after several cycles. Besides, while calcium carbonate always decomposes completely to calcium oxide, CaO derived from natural sorbents rapidly losses its capacity to react of CO_2 and over a number of cycles of reaction with CO_2 its reactivity begins to decay. The conversion of the sorbent CaO to $CaCO_3$ at this transition is defined as carrying capacity of the sorbent or as maximum carbonation conversion and is nowadays well known to decrease as the number of carbonation/calcination cycles increase. Baker was one of the first to study this phenomenon.[9]

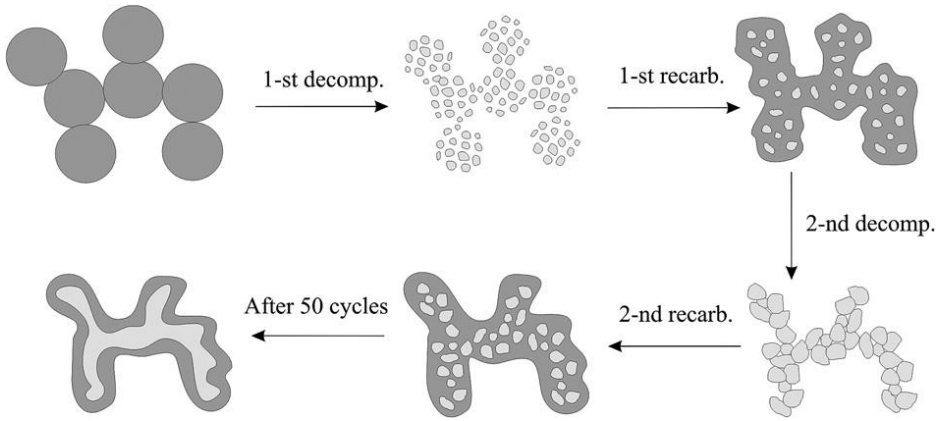

Figure: 8 According to Lysikov et al. schematic diagram of the behavior of limestone after several cycles. [28]

To raise the average reactivity of the calcium oxide in the system, a certain amount of sorbent has to be replaced constantly by a make-up flow of fresh limestone since the sorbent chemically deactivates over time and might some material is lost as fly ash due to attrition. [29, 30] The adding of this make-up flow involves a reduction of the average residence time of the sorbent resulting in a higher carrying capacity.

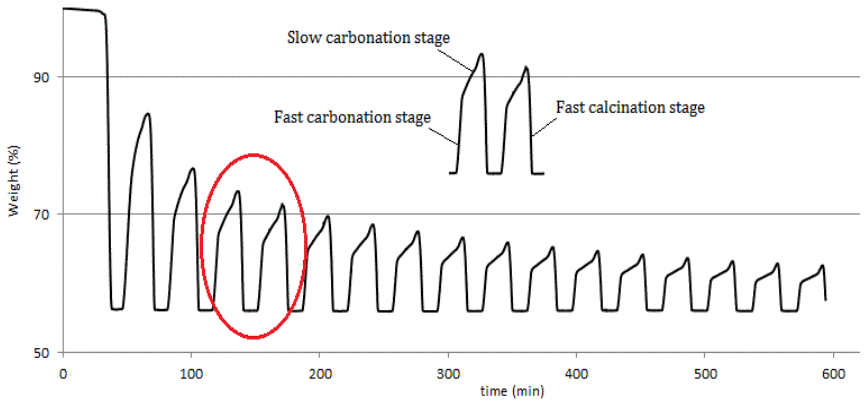

Figure: 9 Weight loss (%) over time

As can be seen in the figure above in carbonation is characterized by a first fast initial rate and after a transition to a slow reaction rate. There have been many attempts to model this decay of carrying capacity / cycles : Abanades, 2002; Abanades and Alvarez, 2003; Wang and Anthony, 2005, 2007; Grasa and Abanades, 2006; Lysikov et al., 2007; Gonzalez et al., 2008.

Grasa and Abanades (2006) after an extended series of trial, find out that there's a residual carrying capacity after 500 cycles. [31] They proposed the following semi empirical equation to describe the loss of reactivity over large numbers of cycles is Equation 2.15:

$$X_N = \frac{1}{\frac{1}{1-X_\infty}+K_N} + x_\infty \qquad \text{Equation 2.15}$$

X_N: the residual carrying capacity

K: the deactivation constant, which increases with more severe calcination conditions

N: number of calcination/carbonation cycles

As an annotation the model proposed, due to is semi-empirical, cannot be used to predict the behavior of individual limestones from their intrinsic properties.

The following equation was proposed for Abanades et. al. to estimate the decay of CO_2 absorption capacity of Ca sorbents.[32]

$$X_N = f_m^N \left(1 - f_w \right) + f_w \qquad \text{Equation 2.16}$$

With the values: $f_m = 0.77$ and $f_w = 0.17$ for natural limestone and X_N the carbonation conversion after N cycles.

Interestingly, even in the worst sever decay of the sorbent CaO, its results of carrying capacity CO_2 are competitive to the carrying capacity of other sorbents that have been studied for CO_2 capture. In small scale tests residual capacity of 1.4mmol CO_2/ g sorbent was found. [30] They have a high theoretical capacity of CO_2 capture (kg of CO_2 absorbed / kg of sorbent). Others carrying capacities sorbents are: MgO-based sorbents 0.5mmol g-1, LDHs-based sorbents with $HCO3^-$, $NO3^-$, $SO4^{2-}$, and Cl^- anions 0.2 mmol g^{-1}. Nevertheless, several studies have been carried out to reduce this withdrawal of capacity because of the negative impact in efficiency and economics of the overall process.

Decrease in absorption capacity can be caused by many different factors. According to several studies, the major case of loss in reactivity comes from the sintering of the porous CaO during the high temperature calcination stage. This sintering causes a reduction in the reactive surface affecting in the drop-off in reactivity.

Sintering of CaO increases at higher temperatures, durations of calcinations, and also with impurities according [9] a collection of several studies : Wang et al., 2010; Manovic et al., 2008a,b; Alvarez and Abanades, 2005a; Manovic et al., 2009; Bouquet et al., 2009; Lysikov et al., 2008; Stanmore and Gilot, 2005.

Others factors that reduce the activity of sorbents are the loss of bed material through attrition of sorbent grains during the process causing elutriation of fines, and chemical inactivation and ash fouling.

2.3.4 Sulfation

Another cause of this deactivation might be due to the competing sulfation reactions.[9]

Most fuels used for combustion processes contain a certain amount of sulfur. This sulfur turns into SO_2 after combustion. This reaction with SO_2 formed during combustion must be taken into account because CaO and $CaCO_3$ have a huge affinity with sulfur according to equation 2.17.

Coal typically contains sulfur in concentrations of 0-8wt.%. SO_2 and CO_2 influence each other to react with lime. Firstly SO_2 reduces the binding of carbon dioxide whereas the continuous cycles carbonation-calcination increase the absorption of SO_2. [33]

Lime-based sorbent can be expected to react irreversibly with SO_2 in combustion applications. Abanades et al. speculated that natural Ca/S molar ratio would be expected to be higher than 20 and the carbonator might also achieve effective SO_2 capture, avoiding the use of desulfurization. The fractional average conversion to $CaSO_4$ is between 0.01 and 0.1 and this lower amount should not prevent the carbonation reaction. [27] However, Sun et al.(2007) using a thermogravimetric proved that SO_2 appreciable deactivates the carrying capacity, the performance of lime-based sorbents .[34]

During simultaneous capture of $CO_2$and SO_2, it is believed that three reactions occur simultaneously: Sulfation, direct sulfation and carbonation.

Sulfation follows this equation:

$$CaO_{(s)} + SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow CaSO_{4\,(s)} \quad AH° = -502kJ/mol \qquad \text{Equation 2.17}$$

It occurs when the partial pressure of CO_2 in the reaction is higher than the equilibrium vapor pressure of CO_2.

Direct sulfation follows the next equation:

$$CaCO3(s) + SO2(g) + \frac{1}{2}O_{2(g)} \rightarrow CaSO4(s) + CO2(g)\; AH° = -324\; kJ/mol \qquad \text{Equation 2.18}$$

It is formed when the partial pressure of CO_2 is lower than the equilibrium vapor pressure of CO_2.

When sorbent regeneration (900°C) $CaSO_4$ remains thermodynamically stable obstructing carbonation during the carbonation-calcination cycles. CaO reacts with SO_2 and consequently cannot react with CO_2 because of the $CaSO_4$ product layer formed in the particle surface. [35]

The $CaSO_4$ formed is in most cases considered useful sorbent irreversibly lost and therefore it is necessary to be replaced. But the use of this sorbent to produce $CaSO_4$ is a good solution for desulfurization.

2.3.5 Attrition and fragmentation

Another problem that presents ca-based sorbents is the attrition.

The particles in the reactor are subject to impacts which can lead to this phenomenon together with breakage. [9] Scala et al. [36] note that both processes: internal stresses originate for the thermal shock and buildup of internal gas pressure and rounding off of the roughness of the particles give rise to fragmentation.

Calcination and sulfation processes have different effects on this phenomenon. It is known that partially sulfated limestone particles are less susceptible to the effects of attrition in a fluidized bed than the fully carbonated sorbent, while calcined materials are the most susceptible to such effects. Therefore, the calciner is prone to present more problems in terms of attrition. Then, partial sulfation can be used as part of the solution for the material loss due to attrition.

3 Sorbent aspects

The sorbent used to carry out the carbonate looping process is lime, calcium oxide (CaO). Silban et al.(1996) and Shimizu et al.(1999) were the first who proposed the use of calcium-base sorbents to capture CO2 from flue gases at high temperatures. His research was based on the reversible reaction: [37]

$$\underset{\textit{Quicklime}}{CaO} + CO_2 \leftrightarrow \underset{\textit{Limestone}}{CaCO_3} \qquad \text{Equation 3.1}$$

3.1 Limestone

Limestone $CaCO_3$ is an abundant natural resource for the production of limes and it is the cheapest and most commonly available industrial chemical. Limestone is known as chemical sedimentary rock. This sedimentary rock contains at least 50% calcium carbonate ($CaCO_3$) usually in the form of calcite or aragonite. It may contain a few percent other materials like considerable amounts of magnesium carbonate (dolomite) as well minor constituents also present as quartz, feldspar, clay minerals, pyrite, siderite and other materials.

Calcium carbonate constitutes one of the main components of marine organism shells, snail shells, pearls and eggshells.[38] Nowadays there exist many environments where limestone is formed –most of them are found in shallow water areas between 30 degrees north latitude and 30 degrees south latitude- Abanades et. Al 2004.

3.2 Formation of limestone

There are two processes in which limestone is formed. Either by ocean-dwelling organisms or by evaporation.

Ocean-dwelling organisms such as oysters, clams, mussels and coral use calcium carbonate ($CaCO_3$) found in seawater to create their shells and bones. When these organisms die, their shells and skeletal are compacted over millions of years settled on the ocean floor as sediment turning into limestone formed by calcite (aragonite is always unstable and is transformed into calcite). [39] Limestone formed from this type of sediment are called biological sedimentary rocks.[38]

The second way occurs when limestone is formed through evaporation in caves. As the water evaporates, the calcium carbonate that was dissolved in the water is deposited on the cave ceiling. Over times this process results in an accumulation of calcium carbonate on the cave ceiling. This is known as a stalactite. If the droplet evaporates once it is on the floor, result in a stalagmite. The limestone in this way of formation is called "travertine" and it is a chemical sedimentary rock. [38, 39]

3.3 Manufacture of Lime

There are few basic steps to perform the manufacture of lime.

1.- The first step of the manufacturing of lime starts with the quarrying of limestone and further mine operations (drying, blasting and conveying broken limestone).

2.- Then, limestone is submitted to crushing and a subsequent screening and classification.

3.- According to the specifications suitable samples of the limestone are sent to rotary kilns to be calcined , subsequently cooled and inspected. These two last steps can be repeated some other times.

Limestone which has become powder is stored as pulverized stone.

4.- Finally, the result obtained as lime is further processes and transferred, storage and submitted to handling operations.

The core of a lime plant is the kiln. Lime is manufactured pursuing one of the next reactions. [40] There is a vast experience handling lime products. [41]

$$CaCO_3 + heat \rightarrow CaO + CO_2 \quad \text{(High calcium lime)} \qquad \text{Equation 3.2}$$

$$CaCO_3 \cdot MgCO_3 + heat \rightarrow 2CO_2 + CaO \cdot MgO \quad \text{(Dolomitic lime)} \qquad \text{Equation 3.3}$$

3.4 Sorbent properties

Calcium oxide is a chemical compound, CaO , a white amorphous solid, caustic, cubic crystalline alkali at ambient temperature. The broadly used term "lime" is referred to all calcium containing inorganic material. By contrast, quicklime is specifically referred to a single chemical compound. [42] Calcium oxide is obtained from the decomposition of calcium carbonate (e.g., limestone) $CaCO_3$. This is accomplished by a thermal reaction, a process called calcination, that consist in heating the material above 850 ° C, to release a molecule of CO_2. The equation 3.1 describes the reverse reaction called carbonation.

There are two forms of lime, quicklime (calcium oxide – CaO) and slaked lime (calcium hydroxide-$Ca(OH)_2$).

Slaked lime is formed by reacting quicklime with water. [43] Quicklime is the one of our interest and we will refer to it in the entire chapter.

Before starting with some properties of quicklime, it is interesting to show some database about lime.

Table: 2 Annual production of lime (calcium oxide and calcium hydroxide).Data from the US Geological Survey, 2012

World	**348 million tonnes**
United Sates	19 million tonnes
Europe	27 million tonnes
Germany	6,6 million tonnes
China	220 million tonnes
Rest of Asia	32 million tonnes

The annual world production of CaO approaches to 348 million metrics tones. China leads the first position as the largest producer in the world.

Products are often ground into pulverized quicklime. When mixing it with additives result in specialized blended composites. Due to the chemical properties of some additives, quicklime can "Fluidized," that is, having properties of being highly fluid. [44]

Quicklime in addition with water forms slaked. It is formed a white powder.

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad \text{Equation 3.4}$$

Slaked lime

Calcium oxide can react with acids to give calcium salts.

$$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O \qquad \text{Equation 3.5}$$

Sulphuric acid *Calcium sulphate*

3.5 Uses of lime, sorbent applications

The lime is a compound widely used today. Because of its easy implementation and deriving from $CaCO_3$, the second material more found on earth, is a good choice to use as a material. Its realization is carried out at very low costs and its properties are suitable for many applications which will be explained below.

Quicklime (Calcium Oxide) is used in the following industrial applications;

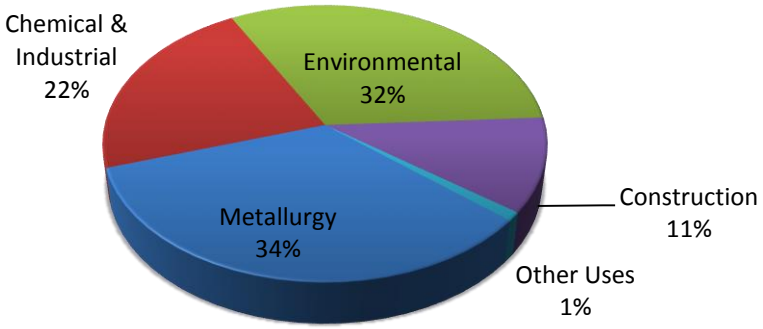

Figure: 10 Information update 2013- Data courtesy of National Lime Association ("Lime Facts" bulletin), U.S Geological Survey ("Mineral Commodity Summaries")

By far, the major uses of lime are given in the steel manufacturing industry and cement making. They are also used in the chemical and construction industries and in agriculture. Environmental application are the fastest growing use where lime is used to comply with air, drinking water and solids waster regulations [45]

On a worldwide basis, the proportions of lime used in different industries are:

A 60% in the metallurgy; Mainly in steel manufacture to remove impurities and its use in the blast furnace. It is used in the iron smelting industry where it acts as a reducing agent at the extremely high temperatures of the blast furnace and in the presence of carbon source. Some other examples are:

-Most extensive use as a flux in purifying steel

-To neutralize sulfuric acid based waste.

-Use in the flotation or recovery of many non-ferrous ores.

-Varying amounts to remove silica from bauxite ore and for causticization in the manufacture alumina.

-Use in electrolytic processes of magnesium production.

A 25 % is used in the construction; Lime is indispensable for use with mortars and plasters and in agriculture it is used for stabilize soils.

According to National Lime Association [46]"Mortars compound with lime and Portland cement exhibit superior workability balanced with appropriate compressive strength, low water permeability and superior bond strength." Quicklime when mixed with sand and water undergoes a chemical reaction involving the formation of $CaOH_2$ resulting in the formation of concrete. This will convert the clays (and other pozzolanic materials) in the soil to a cement type compound. These reactions consume water just as hydrating and curing a Portland cement concrete does. These materials are widely used in Europe.

Finally, approximately the remaining 15% is for chemical and industrial uses; as a reagent in the manufacture of paper, to make precipitated calcium carbonate and in refining sugar.

Also for environmental uses such as: [42, 47]

-Flue gas treatment –remove acidic gases particularly SO_2 and hydrogen chloride-.

-Drinking water treatment. Softening, pH adjustment/coagulation and removal of impurities.

-Wastewater treatment. Industrial wastewater and acid mine drainage.

-Sludge treatment; Sewage biosolids, animal wastes, industrial sludges and petroleum. [45]

Finally some examples are presented of uses in agriculture and food:

-To pH adjustment of agricultural soils.

-In some circumstances its use allows reduced use of fertilizer.

-Used in composting, and certain fertilizers and pesticides.

-In the industry of food limes is used in several processes.

-Baking powder- in baking industry atmospheric storage of fruit and vegetables bags of hydrated lime are placed on racks in the storage room to absorb CO_2.

However this proportion strongly varies depending on the country.

These are just some application for lime, but there is a large variety that in this work will not be extended.

3.6 Use of deactivated quicklime

Spent sorbent can be used as a raw material in cement production in place of the limestone which is the usual constituent for cement feed. Limestone represents approximately 85wt.% of the raw feed. Approximately 1.5 tons of raw materials are required to produce 1 ton of cement.[30]

The purged material may have a proportion of ash and calcium sulfate; the ash could also fulfill some of the cement additives requirements that are usually supplied in the clay (e.g., SiO_2, Al_2O_3, and Fe_2O) and suppose less than 2wt%. [30]

The first step consist in calcine the limestone to achieve CaO to mixt it with other components at high temperatures around 1400-1500ºC in the kiln to produce clinker.

The proportion of sulphur in the final cement affects in its strength properties. But nowadays the sulphur amount can be controlled using kiln by-pass line to remove useless components. Anyway CaO has a strong affinity with SO_2 and a proportion of the CaO in the material will be present in $CaSO_4$.

The advantages of the use of CaO sorbent is that reduce the generation of CO_2 and pollutants. There's a saving in raw materials and fuel and a decrease of gaseous emissions. [48]

Another important use that has been recently investigated [49] is the use of spent sorbent from carbonation-calcination cycles for SO_2 capture, desulfurization.

3.7 Environmental effects of quicklime

Its environmental impact is difficult to assess because it is a non-toxic compound.

The environmental effects of quicklime are minimal when the material is properly used, but it produces also some reactions that can become harmful to the system surrounding it.

An adverse effect is originated due to the vigorous reaction between water and quicklime, quicklime causes severe irritation when inhaled or placed in contact with skin or moist eyes. Additionally inhalation may cause coughing, sneezing and difficulty to breathing. It can result in burns with perforation of the nasal septum, abdominal pain, nausea and vomiting. Control of lime dust during handling of dry lime products should be an integral part of any plant operations involving lime.

Lime is not considered a fire hazard; anyways its reaction with water might release enough heat to ignite combustible materials. [50]

An environment visual impact is that from the quarrying of lime. It results in the destruction of the environment where the quarry is carried out. [51]

Exposure to CaO is regulated. The OSHA PEL (Permissible Exposure Limit) for 8h TWA (Time Weighted Average) is 2mg/m3. The ACGIH also recommends a TLV (Threshold Limit Value) of 2mg/m3 as do fifteen nations.

3.8 Treatments to enhance sorbent absorption

Several researches have been carried out to find out different viable options to counteract this sorbent deactivation. The main goal is increase the porosity area to improve conversion.

The treatments which have shown better results are briefly exposed:

Steam reactivation: According to (Manovic and Anthony, 2010 b,c) raises considerably the carbonation activation (25% to 75%). As advantage the sorbent does not require drying.

Thermal pretreatment: The first who studied the effects was Lysikov et al. As concluding by Manovic et al. (2009) it enhances activity in the initial cycles and is better in sorbents obtained by synthesis than by grinding.

Hydration: Huges et al. [51] proved that hydration of a pre-calcined samples improved the performance of the sorbent for CO_2 capture. However, the main disadvantage of this method showed by Manovic et al.[52] is the predisposition of the samples to fracture what might results in difficulties due to attrition can be intensified.

Natural sorbents: Limestone is composed of calcium and magnesium carbonates and in small extents, composed of impurities, with silica and alumina as the most commons. Limestone can consist of calcite (CaCO3, rhombohedral), aragonite ($CaCO_3$, orthorhombic), dolomite ($CaMg(CO_3)_2$) and magnesite($MgCO_3$). The one with more interest is limestone with a high concentration of calcite due to it allows the highest uptake of CO_2/ unit mass. Regarding SO_2 capture and attrition resistance, huge variation is observed between the different limestones. But regarding to the degradation of reactivity, there's no significant difference.

Doping: Regarding the enhancement of carrying capacity by the use of additives, Fennell et al. proved that addition of small amounts of NaCl and Na_2CO_3 produce improvements in the carrying capacity. [41] However, according to the document of Blamey et al.[9], still none of doping methods have significantly improved the long term reactivity of the sorbent. Also, sale of spent sorbent for use in the cement industry; this option would improve the economics for a calcium looping cycle, due to this integration could decarbonize both industries.

Recarbonation: This method tries to maintain the activity of the sorbent by forcing the limestone particles to increase their conversion above the maximum CO_2 carrying capacity. This method will be later with TGA proved.

4 Setup of the 300kW$_{th}$ pilot plant

The Carina (Carbon Capture by means of an Indirectly Heated Carbonate Looping process) project has been built up in a 300kW$_{th}$ pilot plant in the Technical University of Darmstadt and has recently , during the month of February, been in operation. The first test campaign was carried out on the 9th of February of this year and kept operating for 4 days. High data amount has been collected from the operating duration and subsequently being analyzed.

The test rig consists of three interconnected fluidized bed reactors for CO_2 capture (the carbonator) sorbent regeneration (the calciner) and the heat provider (combustor). The heat transfer from combustor to calciner is provided by heat sodium exchanger pipes. Additionally it has also components for the proper coupling between both reactors calciner and carbonator; one loop seal for the coupling calciner-carbonator and a combination system of L-valve with cone-valve for the coupling in the contrary way. Furthermore another loop seal is used for the internal solid recirculation of the carbonator. Air compressors and air heaters are also components of the system. Both reactors –carbonator and calciner- are equipped with a cyclone integrated in the refractory line because has been studied that even if the velocities of calciner and carbonator are low, there is a certain material entrainment with the gas flow.

Fluidization agents are needed because of the solid flow requirement through the calciner.

The fluids that can be used for steam generation are the flue gas of the carbonator (650°C), the hot CO2 stream of the calciner(900°C) and the flue gas of the combustor (1000-1100°C).

The coupling components of the reactor system, e.g. the standpipes, the loop seal and the L-valve and cone valve combination are manufactured of high temperature steel (1.4878).

4.1 Carbonator

The carbonator reactor captures carbon dioxide in a circulating fluidized bed (CFB) of calcium oxide set to a temperature of 650ºC and at ambient pressure. The following exothermic reaction- equation 4.1- takes place in the reactor.

$$CaO(s) + CO_2(g) \rightarrow CaC0_3(s) \qquad \text{Equation 4.1}$$

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \qquad \text{Equation 4.2}$$

Equation 4.1) The CO_2 contained in the flue gas is absorbed by CaO, resulting in $CaCO_3$ that's transferred to the calciner.

Equation 4.2) When dealing with coal as burning fuel, this reaction has also to be taken into account. An around ~99% SO_2 absorption rate can be assumed for this reaction due to the Ca/S ratio in the carbonator is very high.

The CO_2 fed into the reactor will react with the CaO particles present in the bed. From all the Ca moles contained in the bed reactor only a fraction of the CaO, considered active fraction, reacts with the CO_2. The remaining fraction of the bed particles are considered inactive. [49]

The reactor is fluidized with a synthetic flue gas. Because of the exothermic reaction the cooling of the carbonator has to be controlled otherwise the temperature increases. The heat that has to be extracted from the carbonator depends on the carbonator temperature and the corresponding capture efficiencies. The cooling is performed by means of three cooling lances that are directly situated in the bed of the reactor covering a height of 1.2 m.

The reactor has an internal diameter of 0.25m and height of 8m and is refractory lined

4.2 Combustor chamber

The combustor chamber can be implemented with a Circulating Fluidized Bed (CFB) or with a Bubbling Fluidized Bed (BFB) and is refractory lined. It operates at a temperature of 1000ºC and at ambient pressure.

The heat for the calcination is produced by the combustion of fuel with air and transferred by means of heat pipes. In the 300kWth test rig Carina Plant the fuel is propane.

The combustor is operated with sand, the sand is transferred to the fluidized bed heat exchanger where the heat is directed to the calciner.

The internal length of the reactor is 1.05m, width of 0.3m and height of 2.3m. It is refractory lined.

4.3 Calciner

The calcination reaction is carried on in a Bubbling Fluidized Bed (BFB) at a 900ºC and refractory lined.

The reaction that take places into it:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \text{Equation 4.3}$$

Equation 4.3 is the main reaction. Limestone is calcined to obtain CaO which will be directed to the carbonator, and the released CO_2 will be further stored.

The calciner heat demands an important fraction of the total energy entering the system in order to provide the heat for the endothermic reaction and to heat the incoming gas and solids streams up to calciner temperatures. However this energy can be recovered to drive a high efficiency steam cycle. [53]

There can be two different configurations to set up the direction of the flow going through the calciner; the once-through calciner and the ideal mixt calciner. The once-through calciner allows two flow directions of the sorbent. It's characterized by a low stirred sorbent through the reactor and the temperature profile over the calciner height depends on the partial pressure of CO_2. Otherwise, in the ideal mixt calciner the incoming sorbent is mixed with the whole sorbent content of the calciner. That's why the temperature remains approximately constant over the whole calciner height.

To decide the sorbent and gas flow direction, there are two models; the co-current flow calciner and the counter-current flow calciner.

The co-current flow calciner needs a reduced number of heat pipes due to a lower mean temperature of sorbent in the calciner, what produces a higher gradient of temperatures for the heat transference between the fluidized bed exchanger and the calciner. The drawback is that the temperature of the sorbent at the exit is higher, so more heat consumption is required. In counter-current flow calciner gas and sorbent flow are in counter current flow direction. It provides a lower temperature of sorbent at the exit which implies reduced heat consumption.

In the Carina plant project the solids coming from the carbonator enter the calciner on the top and pass the reactor at first in a countercurrent flow direction and then change to a co-current flow and leave the reactor again on the upper side. The reason why the design combines both configurations flow is the additional bearing of the heat pipes in the middle of the reactor that appears to be necessary due to the length of the heat pipes. So a bending of the heat pipes can be avoided.

4.4 More components /peripherals

The unit is also provided of two loop seals for the proper coupling between reactors, one is placed in the outlet of the carbonator after the cyclone. The second one handles with the solid recirculation from the carbonator. They offer very accurately adjustable and continuous material transport and good pressure seal between reactors. Both loop seals have two exists to allow the deviation of particle circulation. Also the combination among the L-valve and L-cone valve is placed in the way from carbonator to calciner to provide the required pressure seal.

The cyclones separate the solids from the flue gas, in the case of the carbonator the cyclone separates the carbonated solids from the CO_2 depleted flue gas and the solids follow its way through the standpipe below the cyclone. Then the solids depending on the solid flux through the calciner and the entrained solid flux from the carbonator are feed or to the internal recirculation loop seal of the carbonator or directed to the calciner flowing first throw the L-valve L-cone combination to control the pressure. In the calciner the solid flow separated in its corresponding cyclone falls down through a refractory lined standpipe into the corresponding loop seal which is fluidized to recycle the particles back to the carbonator.

To fulfill the requirements the air flow entering the reactors must be heated up that for what heating devices are installed in the fluidizing gas pipe.

The primary air supply of the reactors is provided by a compressor with a distribution for three primary air paths (one for each fluidized bed). It is built in order to assure the pressure drop that they generate to be high enough to ensure the proper regime in the reactor for the solid inventories fed into the system. Moreover, each path has its own electrical air preheater to control the reactor temperatures.

Furthermore an air quench unit is installed to cool down the flue gases leaving the reactors. Fresh air is drawn through the quench air supply pipes and mixed inside the quench units with the flue gas to mixing temperatures below 250°C. After this process the streams are mixed in a main gas header.

5 Simulation process with Aspen PLUS

In this chapter will be discussed the model of Carbonate looping process in Aspen Plus together with the description of its features. Furthermore the model 300kWth in Aspen Plus will be analyzed with real data extracted from the first measurements of the Carina pilot plant, compared and studied.

5.1 Aspen Plus development

The carbonate looping process has been developed in many occasions with Aspen Plus at the TU Darmstadt. Aspen Plus is the market-leading chemical process optimization software used by chemical industries.

At this point will be briefly described the layout and the main characteristics of Aspen PLUS model. It has to be mentioned that an extend Fortran language has not been used to develop the carbonate looping model in Aspen Plus. In this case is not required for the performed study. Furthermore the model has been built with the software taking the reference from a former model built years ago.

Two different models, referring to a different used fuel for the indirectly heated calciner in combustor, have been performed to the study of the carbonate looping.

One model uses propane as fuel and the other coal. The first one will be of special interest due to it is underway at the TU Darmstadt a 300kWth carbonate looping process with indirectly heated calciner using propane. Thereby the model attempts to reflect the most the real process.

The model in Aspen Plus consists of three main reactors representing the fluidized beds; carbonator, calciner and combustor, moreover peripheral compounds such as filter, compressor and heat exchangers are also going to be further explained.

5.1.1 Stream Classes

To get a basic idea of stream classes in Aspen Plus and thus naming them in the future directly with the name of the stream class, will be present a brief summary of stream classes.

MIXED- it does not contain solids, it is a stream considered only in vapor phase.

CIPSD – Conventional Inert Particles Size Distribution. It is used in streams with conventional inert solids and can be defined a particle size distribution.

NCPSD- Non Conventional Particles Size Distribution. It is defined when dealing with non-conventional solids. In this work it is going to handle with Ash and Coal as non-conventional solids. In each case, they must be properly defined.

To conclude this paragraph in the content of stream classes, all Aspen plus model is defined in MIXNCPS stream class. This means that the model accepts MIXED, CIPSD and NCPSD stream classes.

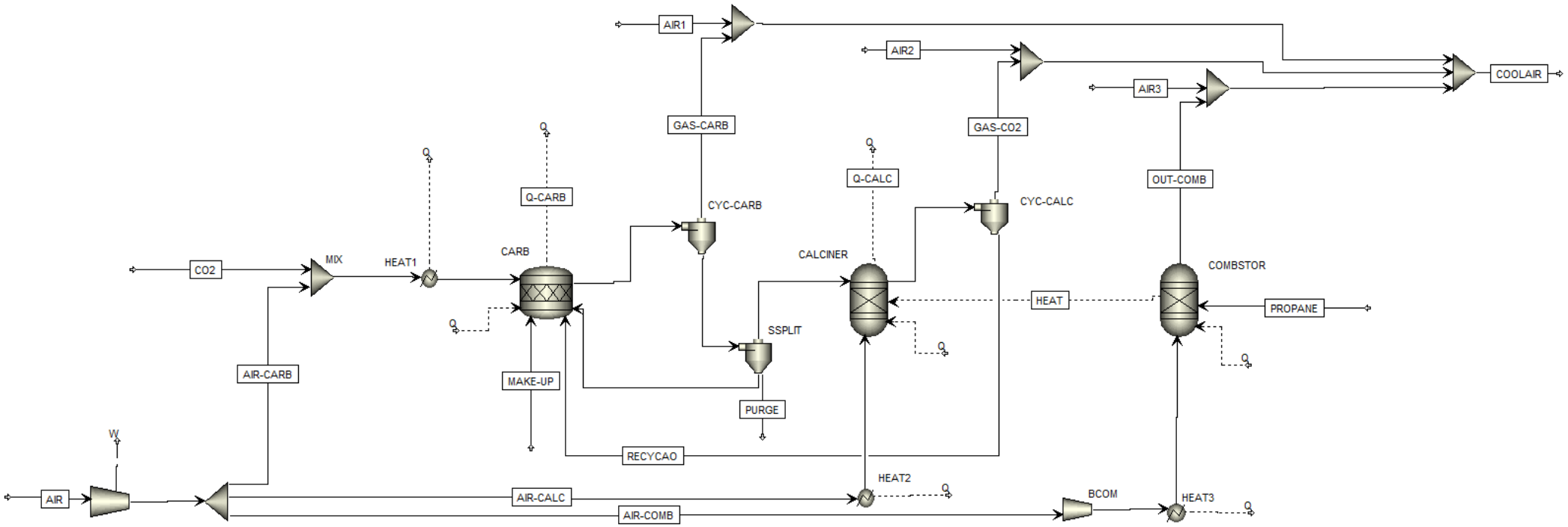

Figure: 11 Propane model with Aspen PLUS

5.1.2 Carbonator

The carbonator – CARB- is represented by the reactor RSTOIC. This reactor is suitable when the reaction stoichiometry is known but information on kinetics is not available or not so important. This reactor is well defined with the equation, the predetermination of molar conversion of the sorbent, CaO, and must be defined a temperature and a pressure inside the reactor, this values are respectively 650°C and 1.013bar.

The main feed stream on the reactor is the flue gas from the power plant which, in the model, contains CO_2 and air. Another inlet stream is the make-up, compound of limestone, to compensate the deactivation of the sorbent. In this model is placed in the carbonator but because of in the Carina project is located in the calciner, this stream will be analyzed in both situation. A stream with the recirculated solids from the calciner is also feeding the reactor, thus achieving the looping process. The output stream containing mainly air, CO_2 depleted stream and solids CaO and $CaCO_3$ is directed to a first cyclone, which separates the mixed –vapor phases- (CO_2, N_2, O2,…) from the solids -CIPSD, that continue their way to the calciner. There is also an output heat stream –Q-CARB- going out from the carbonator which represents the necessary cooling of the carbonator since the reaction that takes places in it is exothermic. In a later chapter is studied under what conditions is altered this heat value. In the reactor is set the molar conversion of the sorbent, which its impact is also going to be studied in a further chapter.

Additionally, another heat stream is added in the carbonator representing the losses of the reactor.

5.1.3 Calciner

The calciner –CALC- is represented with a RGIBBS reactor since the end products are known. This block does not require exact information about the stoichiometry or kinetics. The reactor is well defined once specified temperature, pressure and it is advisable to specify the components that take place in the calcination process in the reactor.

The calciner is set at a temperature of 900ºC and atmospheric pressure

The main inlet stream in the calciner is the one containing solids –CaO and $CaCO_3$ - coming from the carbonator after having been filtered by the first cyclone.

An air stream flue gas is entering into de calciner to fluidize the bed reactor. In section 5.2.2 the minimum incoming air is analyzed for that proper fluidization occurs.

The stream leaving the calciner is directed back to the carbonator. But first is filtered by a cyclone where again MIXED stream –vapor phases- and solids are separated.

Since the reaction occurring in the reactor is endothermic a heat source is needed to cover the energy needed for this reaction to take place. This heat is supplied by the combustor through heat pipes. The heat pipes are represented as an inlet heat stream in the calciner –HEAT-.

5.1.4 Combustor

To represent the combustor the reactor Gibbs is considered the most suitable. Its calculations are based on minimizing the Gibbs energy for the system and it is not necessary to provide detailed stoichiometry or yield.

The combustor is set at 1000ºC and 1.013bar.

The inlet streams are the chosen fuel and the air necessary to produce the required heat combustion to provide to the calciner through heat pipes. Using a Calculator, the air required is calculated in each case to successfully complete combustion.

The outlet stream is all vapor phase, which depending on the used configuration is directed to compression or redirected to the carbonator. It will be seen in detail below. Another outlet stream is the one representing heat pipes, which is directed to the calciner to provide the required heat.

Additionally, as in the calciner, a heat stream is added into the reactors to represent their losses.

5.1.5 Auxiliary powers

So far has been explained the bulk of the system, the three reactors that constitute the core of the model, but there are more components in the model that cannot be forgotten because they play an essential role to represent the system with the best accuracy. These components are briefly described below.

SSPLIT'S: This component acts like a filter and depending on the established setting the mass flow will be diverted and directed to the desired direction. The model contains two Ssplit components named –CYC-CARB and SSPLIT-. The first one is basically a cyclone; it separates the vapor flue gas from the solids and at the same time allows the setting of the mass flow of the recirculating solids that means to set the amount of solids circulating in the system. The next one offers three streams to direct the solids. Some solids are going to be directed back to the carbonator, to the calciner or put away as purge. Because of the purge the make-up flow is necessary to maintain a flow mass in the system. The fraction of the amount of mass flow directed in each stream is settled in this compound.

COMPRESSOR: The compressor-COMPR- is located at the beginning of the system. It is fed with a stream of air which its amount has to be the sum of the air mass flow inlet needed in the three reactors. The inclusion of the compressor is because the drafts during their way to the reactors may possibly suffer a loss of pressure such

that upon reaching the reactor would not have enough pressure to enter. Pressure drop occurs when frictional forces caused by the resistance to flow act on a fluid through the tube. Thus, the compressor increases the air inlet streams around 200mbar pressure for even having a pressure drop, any problem of air to get into the fluidized beds occurs.

HEAT'S: On the one hand, the inlet air streams are heated up before to take contact with the reactor. The inlet air flow rate entering the carbonator is heated up to 250ºC and the others streams directed to calciner and combustor are heated up to 500ºC.

MIXER**:** For the air cooling and the distribution of the air inlet the component Mixer is necessary to a proper distribution of them.

5.1.6 Design Specs

CONV: Its aim is to establish the CO_2 capture efficiency in the carbonator. Is a simple specification where is set the CO_2 amount in the outlet of the carbonator to be (1-conv) from the CO_2 in the inlet, being –conv- the desired capture efficiency. The SSPLIT regulating solid circulating varies in order to achieve this specification.

HEAT: The combustor is required to transmit to the calciner a necessary heat in order to let the calciner perform its function properly. Varying the duty of the combustor between a range is aimed the heat from the calciner to be zero. Thus, the aim is to achieve the necessary duty in the combustor in order to get the heat pipes to be the only source of heat to the calciner.

PROPANE: To vary the propane mass flow in order to get a temperature outlet in the carbonator of 1000°C.

5.1.7 Calculator

With the next combustion reaction and air excess of 1.2 by means of FORTRAN language is set up the necessary air depending on the required amount of propane in every situation.

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \qquad \text{Equation 5.1}$$

In practice is almost impossible to get a homogeneous and total mixture of the combustible with the carburant -air in this case-. This forces to use a greater amount of air than the stoichiometric in order to produce combustion as complete as possible.

5.2 Propane Model

The parametric study consists in a brief analysis, pointing out the most important factors that influence the variation of system in model Aspen Plus. The aim of this chapter is to acquire and overall knowledge of the influence of each parameter in the system and the dependence between them.

In reality, most of the parameters, because of being inlet parameters, can be varied by the operator, but in other cases; when focusing in the molar conversion of the sorbent or the CO_2 capture efficiency, doesn't depend directly on the operator who manages the inlet parameters.

The study is going to be performed with Aspen PLUS Software; in this case, it is not only possible to specify the inlet parameters as are: air inlet into the reactors and combustible mass flow, but it is also possible to define the desired activity of the sorbent and the CO_2 capture efficiency in the carbonator. In fact, it is necessary to fix these variables to allow the program work suitable and get goods results.

In this work the main study will be performed varying:

-The molar conversion between 0.1 and 0.3.

-The CO_2 capture efficiency between 70% and 90%.

-Make up flow will be considered 1% of the CaO solid mass flow recirculated to carbonator.

Many variables are going to be studied regarding these two variables, for what a previous understanding will help to a posterior analysis of the results. For this reason this study will start analyzing the effect on the system of CO_2 capture efficiency of the carbonator and molar conversion of the sorbent.

Moreover, the combustor reactor is settled with a very specific condition. The combustor is dependent on the behavior of the calciner since it exists to provide the heat necessary to the calciner to achieve complete calcination. So the combustor will be later analyzed, due to once the specifications of the calciner are known the analysis of the combustor will be easier to interpret.

5.2.1 CO_2 capture efficiency and molar conversion of the sorbent

The CO_2 capture efficiency is defined as the fraction of CO_2 in the flue gas that is absorbed by CaO in the carbonator. It is known that the CO_2 absorption by CaO is a reaction of first order and as will be seen it depends on the following variables: The circulation of CaO between reactors, the active fraction of CaO that is related to the make-up flow and the solid inventory of the carbonator.

On the one hand, one of the important variables to achieve high capture efficiencies is the flow of CaO coming from the calciner. As is depicted in the following figure -Figure: 12- as the CO_2 capture increases, increases the solid circulating entering the carbonator, being these solids in greater amount CaO.

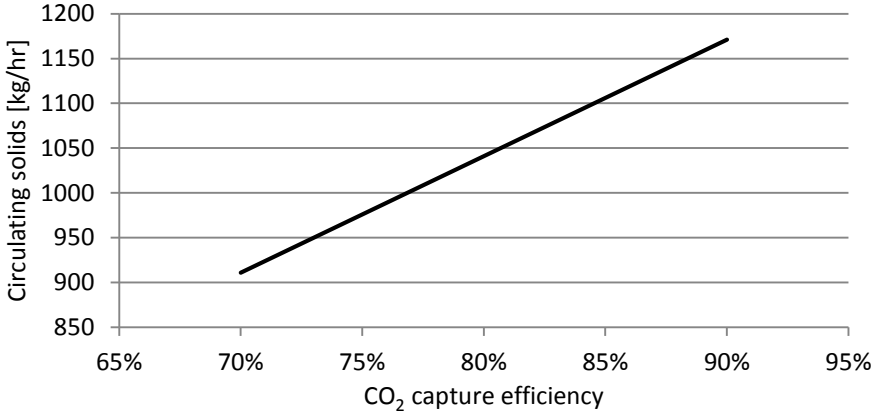

Figure: 12 Circulating solids over an increase of CO_2 capture (0.2 molar conversion)

To achieve the defined CO_2 capture a variation of the circulating solids in the system is necessary due to the molar conversion of the sorbent is a fixed value. Thus, the solid circulating rate between reactors is adjusted to maintain the desired carbonation efficiency.

Moreover, when fixing the CO_2 capture, in this case in 80%, and while increasing the molar conversion of the sorbent, less CaO is needed to be recirculated within the system. This occurs due to the active fraction of CaO rises for what less CaO needs to be cycled to keep the predefined capture efficiency in the carbonator. This effect can be observed in Figure 13.

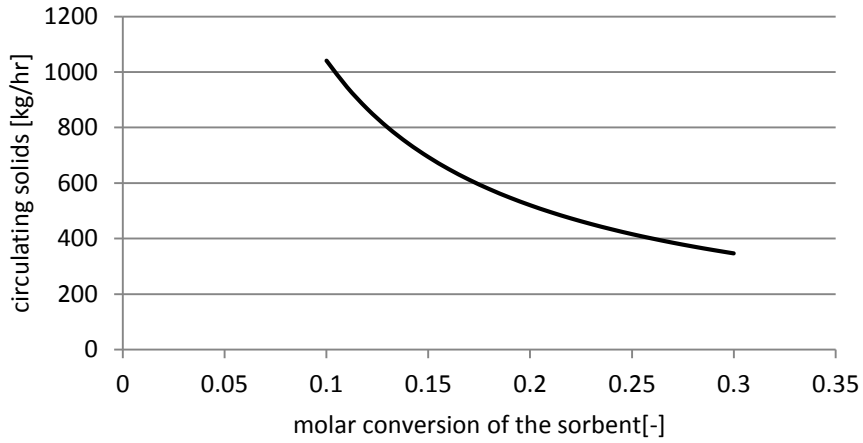

Figure: 13 Circulation solids over molar conversion of the sorbent with 80% capture CO_2.

The solid flow is inversely proportional to the average activity of the sorbent, which is at the same time affected by the value of the limestone make up flow. But in this case, the make up has been fixed on 1% of the

CaO circulating solids between reactors, thus make up development over an increase of the molar conversion of the sorbent will follow the same line as circulating solids.

Another observation is that the change of the molar conversion between low conversions -from 0.1 to 0.2- has a higher decrease of the circulating solids –presents a higher slope- than in the change between higher conversions -from 0.2 to 0.3- due to the reaction mechanism of carbonation.

5.2.2 Carbonator cooling

The parameter that is going to be analyzed next is the carbonator cooling. Without this component in the system, because of the exothermic reaction that is carried out into the reactor, the temperature in the reactor would progressively increase. Therefore a steam generator extracts the excess heat -Q-CARB- resulting from the exothermic CO_2 capture reaction in order to keep the optimum carbonation temperature of 650 °C.

The carbonator cooling affects the total efficiency of the system, as more heat is necessary to be extracted from the carbonator, more can be used in steam generation.

Our aspen model is based in a 300kWth of thermal power of flue gas. As can be intuit there is a huge influence by the power thermal of flue gas with respect to the carbonator cooling. The more thermal power is set more combustible mass is needed to satisfy the conditions of the system. Thereby, the next table points out the mass flow rate of the necessary synthetic flue gas depending on the thermal power of flue gas. The synthetic gas entering the CFB consists of CO_2 and air. At the same time regenerated CaO flows from the double exit flow seal through the cone valve and enters the CFB carbonator where CO_2 is absorbed from CaO. This flow mass is also increasing as the thermal power of flue gas increases.

Table: 3 Mass flow rate of synthetic flue gas for different thermal power flue gases. Values extracted from the excel of energies balances –CARINA Auslegung -1m -provided by the department EST

Thermal power flue gas [kW]	CO_2 synthetic flue gas [kg/hr]	Air of synthetic flue gas [kg/hr]	Circulating solids [kg/hr]
300	102.13	412.91	1041.09
200	68.088	275.27	694.06
150	51.07	206.45	520.55
100	34.04	137.64	347.03

In the next graph is depicted de evolution of the necessary carbonator cooling along the increase of the thermal power of the flue gas and along carbonation efficiency considering 80% of CO_2 capture and 0.1 molar conversion of the sorbent.

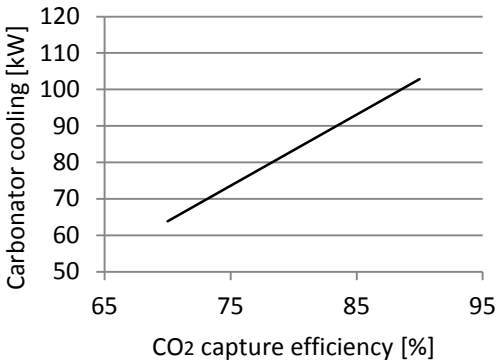

Figure: 14 Carbonator cooling [kW] depending on the thermal power of flue gas [kW]

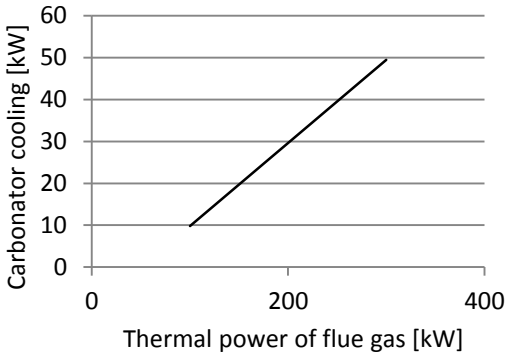

Figure: 15 Carbonate cooling along an increase of CO_2 capture. 300kWth 0.2 molar conversion

The excess heat resulting from the exothermic CO_2 capture reaction increases by increasing the thermal power of flue gas. This is due to an increase of the thermal power flue gas results in, as previously discussed, an increase of the main inlet flow rate mass, thereby increasing the circulating solids flow entering into the carbonator at high temperatures. This increase implies an increase of the average temperature in the carbonator, increasing the carbonator cooling power. Likewise, the increase of circulation solid mass flow caused by the improvement of carbon capture causes the same effect deriving in the same conclusion.

Something similar happens when the carbonator cooling is analyzed over the molar conversion of the sorbent. As seen before, with the increase of the molar conversion of the sorbent, a decrease of the circulating solids is produced –Figure: 13-. For this reason the carbonator cooling will decrease with higher molar conversion -Figure: 16 - since less circulating solids are involved and less heat extract of the carbonator is necessary to compensate the exothermic reaction.

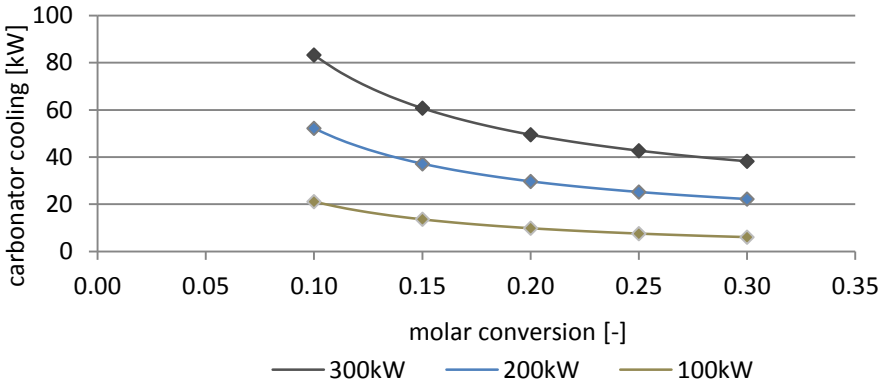

Figure: 16 Carbonator cooling [kW] Vs. molar conversion of the sorbent at different thermal power of flue gas.

Another determining factor is the temperature of the carbonator.

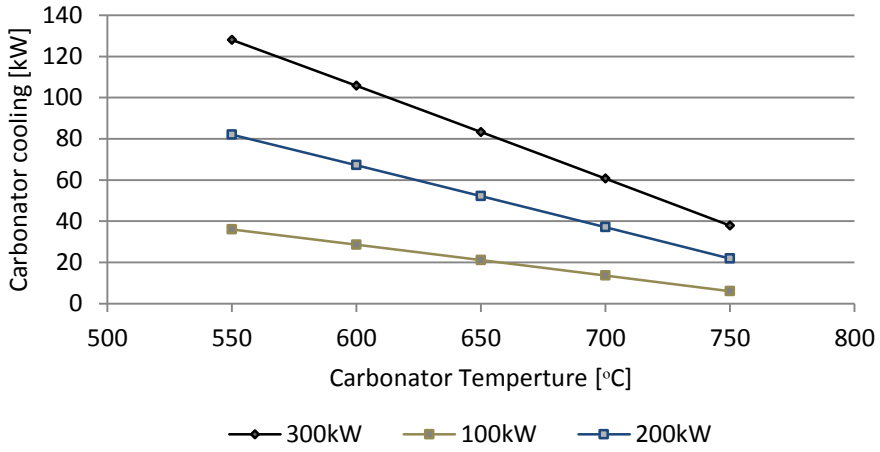

Figure: 17 Carbonator cooling over different carbonator temperatures [°C]

The higher the temperature in the carbonator is the lower the power of heat removal system thereof. The solids entering the calciner are at a temperature around 900 ° C so that the more temperature the carbonator has, more closer will be to the temperature of the solids entering the carbonator thus less heat will be extracted to achieve the desired hold temperature of the reactor.

It is also noted that as the thermal power of flue gas decreases, the variation of the total heat necessary is becoming less significant because of the influence in the amount of recirculating solids, as they decrease, change becomes less significant.

The same way happens when a heat exchanging between the solids circulating is carried out, the so called – solid preheating-. There is an exchange of heat from the carbonator to the calciner and the solids circulating on the way back. Taking into consideration all the explained above as the heat exchange increases, the carbonator cooling decreases due to the decreasing temperature difference between the recirculated solids mass flow and the reactor.

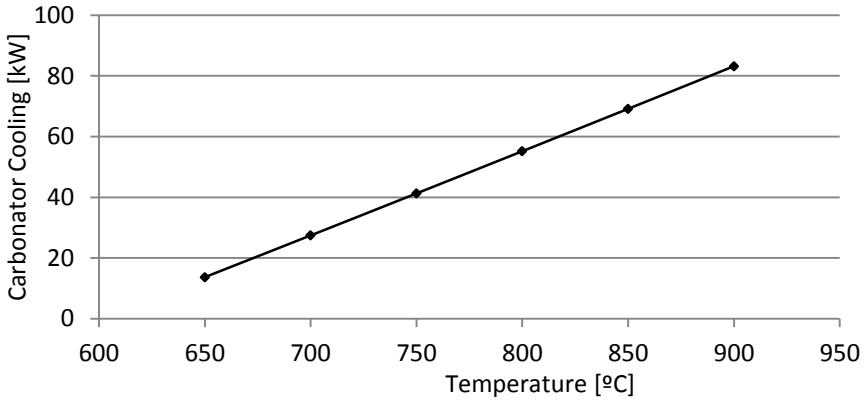

Figure: 18 Cooling carbonator at different temperatures of the recirculating solids inlet mass flow of the carbonator.

5.2.3 CO_2 concentration in outlet gas from calciner

With the increase of the molar conversion fewer solids are circulating among reactors, what can describe this decrease on the CO_2 concentration of the CO_2 rich outlet gas from the calciner. With the lowering of active sorbent more circulating solids are needed. Since make up flow is considered 1% of the total amount of the circulating solids, this act will imply more limestone entering the calciner thus producing more CO_2 concentration in the outlet gas of the calciner. Figure: 20

In the same way, the increase of carbonation efficiency provokes more amount of limestone entering the calciner causing the increase of CO_2 concentration in the calciner outlet flue gas.

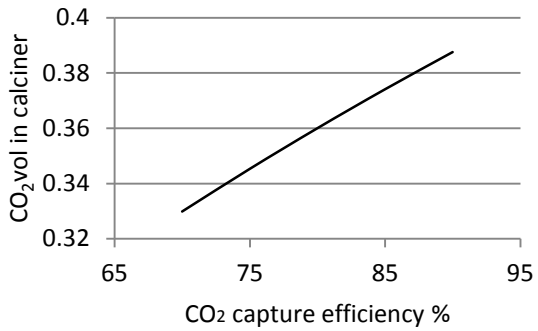

Figure: 19 CO_2 vol% Vs. CO_2 capture efficiency

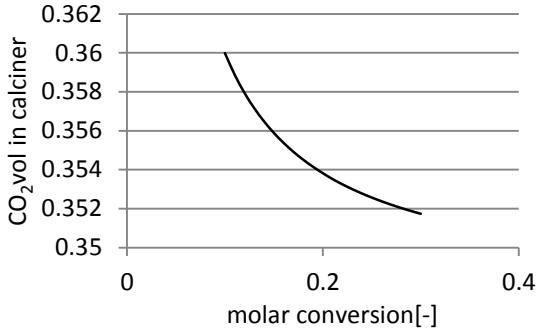

Figure: 20 CO_2 vol% in calciner Vs. molar conversion

5.2.4 Thermal power of combustor and heat pipes

The combustor has to provide the enough heat via heat pipes to the calciner in order to get a complete calcination in the calciner. For this reason depending on the amount of solids entering the calciner, the combustor will need different thermal power.

Regarding what has been previously said about the decrease in molar conversion of the sorbent involving higher circulating solids in the system; the thermal power of the combustor then will increase with the decrease of molar conversion. As more solids enter the calciner more heat is needed to achieve the whole calcination whereby more amount of fuel is necessary to, through the combustion, supply the required heat. Figure: 21 corroborates this explanation.

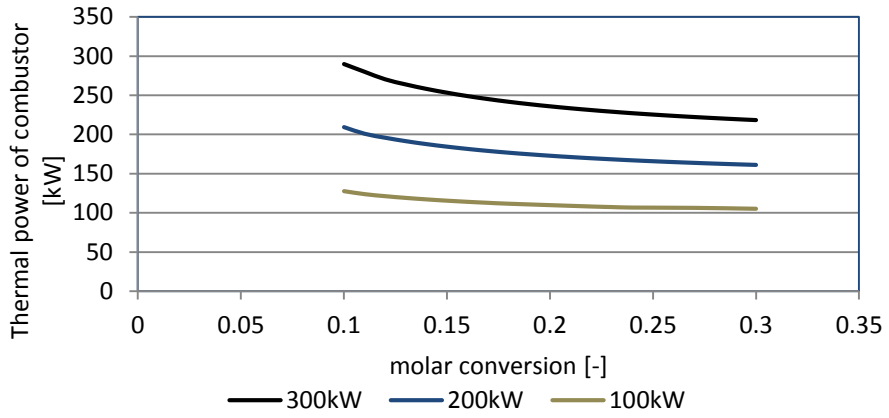

Figure: 21 Thermal power of combustor [kW] Vs. the molar conversion for different thermal power of flue gas.
80% carbonation efficiency.

As the thermal power of flue gas decreases, the thermal power of the combustor varies in a minor proportion due to less solids are subsequently involved. Also following the same pattern as in Figure: 13- solid circulating Vs. molar conversion- there is a more significant slope between the change from 0.1 to 0.2 molar conversion of the sorbent than between 0.2 to 0.3.

Heat pipes power show the necessary heat to transfer from the combustor to the calciner by means of heat pipes. They are directly related with the combustor thermal power and follow its same pattern. So the next graph provides a necessary idea of the power needed by heat pipes depending on their thermal power of flue gas. As the thermal power of flue gas increases, more heat is required to achieve the complete calcination of all solids in the calciner.

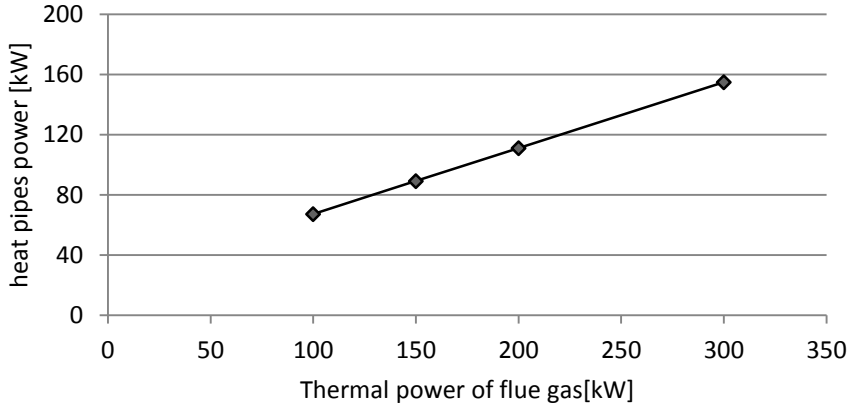

Figure: 22 Heat pipes power [kW] over thermal power of flue gas [kW]

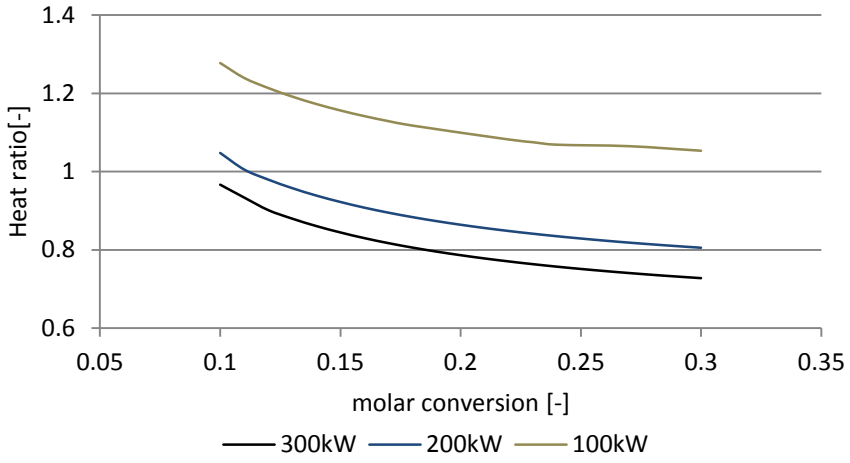

Figure: 23 Heat ratio over molar conversion of the sorbent with different thermal power of flue gas [kW]

The Heat ratio is defined as the thermal power of the combustor divided with the thermal power of flue gas. Here is shown how as the thermal power of flue gas and thermal power of combustor do not grow at the same rate as the thermal power of flue gas is increasing. The thermal power of the combustor grows slower, for that reason, at 100kW they are almost the same value -resulting in a heat ratio around 1- and in 300kW the values have acquired a big difference.

5.2.5 Make up flow

As has been explained in chapter 2.3 -Deactivation of the sorbent-, the activity of the sorbent falls with increasing number of cycles. Depletion of the reactivity of the sorbent is influenced by sorbent sintering, pore closure and reduction of the reacting surface area, competing reactions of the sorbent with sulfurous compounds and ash fouling but the average carrying capacity can be solved iteratively from the make-up flow and overall looping ratio. So, to maintain the activity of the sorbent through the cycles it is necessary to introduce a fresh sorbent. Furthermore as a consequence of adding make up flow the introduction of a solid purge in the calciner is necessary to avoid deactivated sorbent being accumulated.

The make-up flow mass is an important parameter to determine a proper operation of the model. It influences significantly on the CO_2 capture of the system and affects directly the average activity of the sorbent as commented in previous chapters.

Studies so far have been carried out with an addition in the carbonator of limestone of the 1% of the recirculated solids. According with its definition, with an increase of the molar conversion, i.e. activity of the sorbent, the make-up flow necessary should decrease due to not such amount is necessary to fulfill requirements.

However, in this study the progress of the make-up flow over an increase of the molar conversion is clear because it follows the pattern of the solid circulating. Because of in the Aspen PLUS model program the molar conversion of the sorbent is necessary information in order to a proper operating of the model, the study of how make up affects the improvement of the molar conversion cannot be seen in this work. The solid circulating within the system and its development along the increase of molar conversion are indicative data to the fact that as more molar conversion less circulating solids are necessary to achieve the conditions of the model.

The circulating solids amount is regulate according to the requirements of CO_2 capture. When the activity of the sorbent increases less amount of circulating solids is necessary to accomplish it because the sorbent itself has more efficiency.

In following lines, it is going to be studied the influence of the make up on the whole system.

To carry out this analysis the CO_2 capture and the molar conversion of the sorbent have to be fixed. They will have a value respectively of 80% and 0.1.

In the following graphics is presented how a variation of make up flow mass varies the concentration of CO_2 in the outlet flue gas of the calciner and the efficiency. It is going not just to be studied the affection to its parameters, but also depending on the component of the makeup -limestone or quicklime-. The make-up mass flow rate influences significantly in the final composition of the flue gas going out the calciner and in the necessary heat to transfer via heat pipes to the calciner, and then subsequently in the amount of thermal power of the combustor.

The make-up flow enters the carbonator at an ambient temperature. As more make up flow enters the carbonator, less heat exchanger of the carbonator to cool it down is necessary due to the decreasing average temperature of the carbonator -of the total amount of solids involved into the carbonator.-Figure: 24-The circulating solids remain constant. The model itself stables the necessary amount of circulating solids in the system. The majority of the solids recirculating from the calciner are CaO, and the model varies its solids circulation –CaO- depending on the efficiency pursued of CO_2 capture. So even if more make up – limestone- is added, the circulating solids will remain a constant because the same quicklime is needed to enter the carbonator. Contrary, if quicklime is added into the carbonator as make up, then in this model a reduction of the solids coming from the calciner will be produced because part of the quicklime is being provided by the make-up. In both cases, adding limestone or quicklime in the carbonator will reduce the Q-carb necessary because they will reduce the average temperature of the solids entering the carbonator.

Normally without a fixed value of molar conversion of the sorbent, when low make up is added into the carbonator, the modest activity of the sorbent is offset by high solids flow between reactors to maintain the desired carbonation efficiency. [54]

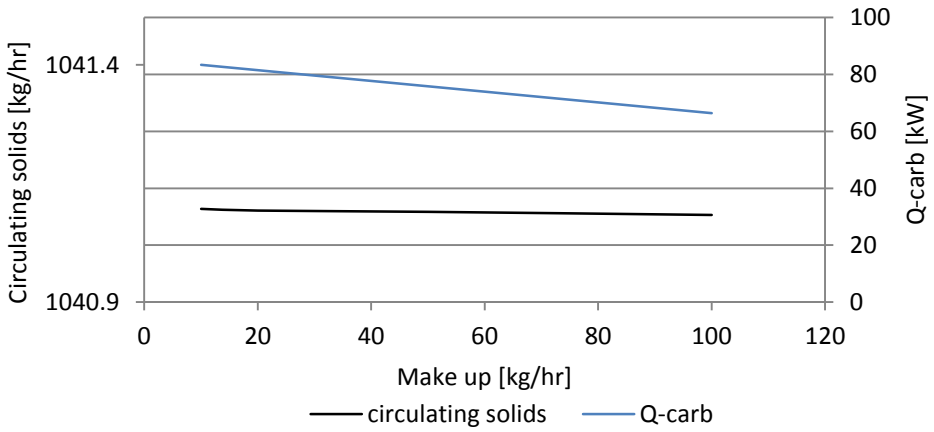

Figure: 24 Carbonator cooling [kW] and circulating solids varying make up CaCO3 [kg/hr] in carbonator.

With an increasing of the make-up flow, for a fix value of CO_2 capture efficiency and of molar conversion of the sorbent, the efficiency decreases whereas the concentration of CO_2 in the calciner gas outlet increases. Figure: 25. As more make-up of limestone is added into the system, more limestone is entering into the calciner, taking part into the calcination reaction, increasing the CO_2 as product, but also the necessary heat of the combustor, decreasing in this way the efficiency.

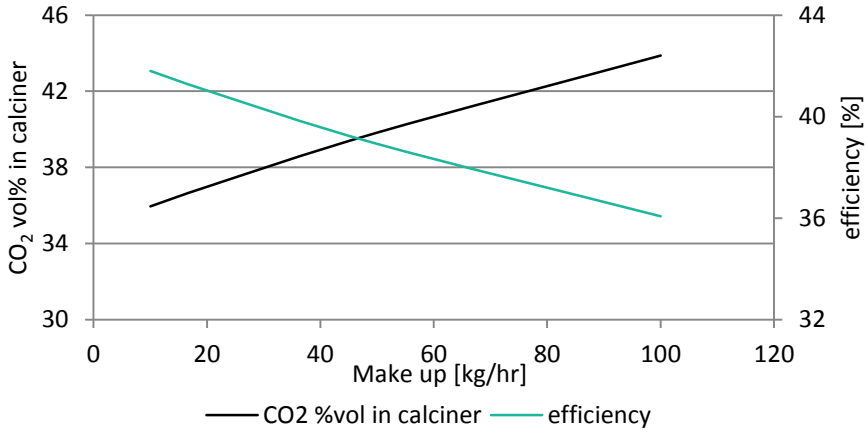

Figure: 25 Efficiency and CO_2 vol% in calciner along variation of make up flow [kg/hr] Molar conversion 0.1 constant. 80% capture

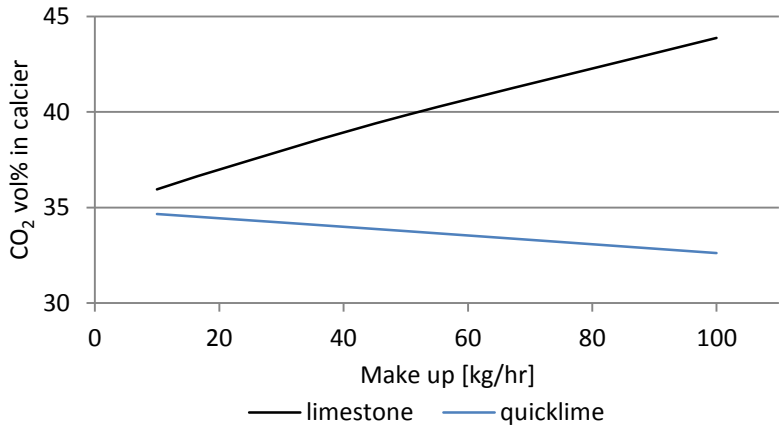

Figure: 26 CO_2 concentration in the outlet flue gas from the calciner over an increase of make-up mass flow [kg/hr] regarding if limestone or quicklime in carbonator

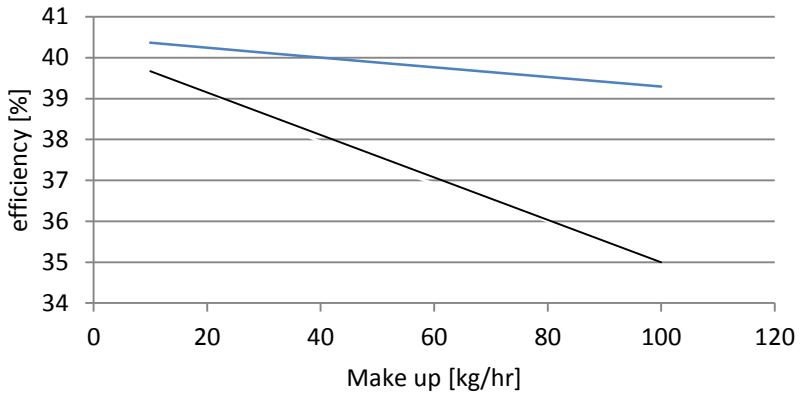

Figure: 27 Efficiency [%] over quicklime make up in added in carbonator or calciner. In blue quicklime and in black limestone.

For the same values of capture efficiency, the CO_2 rich stream composition strongly depends on the $CaCO_3$ make up flow owing to the additional CO_2 released during its calcination.

As can be seen, the use of quicklime as make up in carbonator (the same happens in the calciner) doesn't affect significantly neither in the efficiency nor in the CO_2% volume in calciner. Another important result that stands out is that the use of quicklime as make-up gives always higher efficiency than with limestone. In contrast, the flue gas rich in CO2 going out from the calciner get much higher results with this last.

In several studies limestone is used as make up flow. According to the Figure: 26, whether in the carbonator or the calciner, the more $CaCO_3$ it is added more CO_2 will be on the composition of the gases CO_2 in calciner output. This is because the more the available $CaCO_3$ for calcining, more product amount will give the reaction -CO_2 and CaO-. For identical values of CO_2 capture efficiency, Qrich,CO_2 strongly depends on the $CaCO_3$ make up flow owing to additional CO_2 released during its calcination.

The adding of limestone into the carbonator as make up involves that more fresh limestone needs to be calcined first. Part of this energy can be recovered but the reaction enthalpy of the extract CaO is lost for the process and cannot be used for the power generation.

Moreover, wherever where the make-up mass flow rate is found -in any of the two reactors-, as we increase the mass flow rate of make-up, the higher the required thermal power of combustor to perform its function. This is because more limestone will be calcined and subsequently more fuel required.

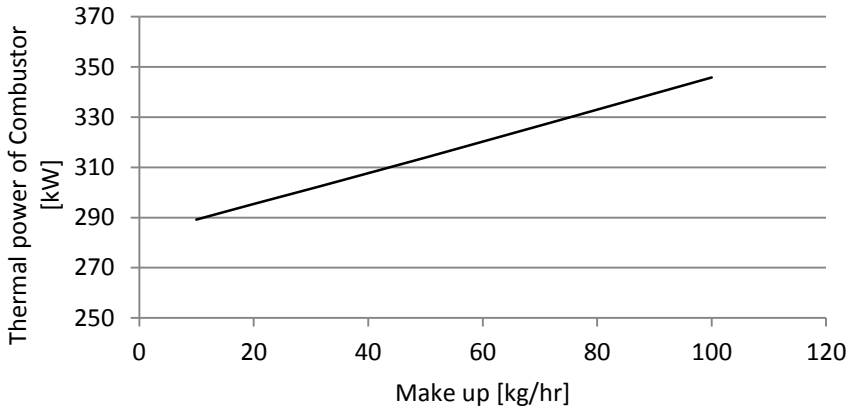

Figure: 28 Thermal power of combustor [kW] Vs. Make-up mas flow [kg/hr]

When quicklime is added into the carbonator, as explained before, less solids are need to recirculate back to the carbonator, for what less solids are taken part in the calciner, reducing the power thermal of the combustor.

In the reality this study cannot be performed due to there has been working with two variables fixed which cannot be fixed for the operator. For this reason, an increase of make-up will not remain stable the molar conversion or the CO_2 capture, and the results will vary compared with these here obtained. Even so, this study gives the reader a brief overview about the influence of make up in the system, having the CO_2 capture and molar conversion fixed.

Normally low make up flow values translate into higher solid circulation rates between reactors. In lot of articles can be read that an increase of the make-up flow induces a rising of the active fraction of CaO so that less CaO needs to be cycled to keep the predefined capture efficiency in the carbonator. However, in this work, as can be seen in Figure: 24 no decrease takes place, because the molar conversion is fixed and there is no possibility to improve the sorbent activity thus maintaining the value of circulating solids mass flow.

5.2.6 Efficiency

Regarding the picture depicted of the Aspen Plus model of propane, the following steps are followed to calculate the efficiency of the system.

Table: 4 Key data of reference power plant

Thermal power	**MWth**	**2308**
Gross electrical power	MWel	1100
Net electrical power	MWel	1052
Auxiliary electrical power	MWel	48
Efficiency	%	95
Useful Thermal power	MWth	2192.6
Factor	%	50.7%

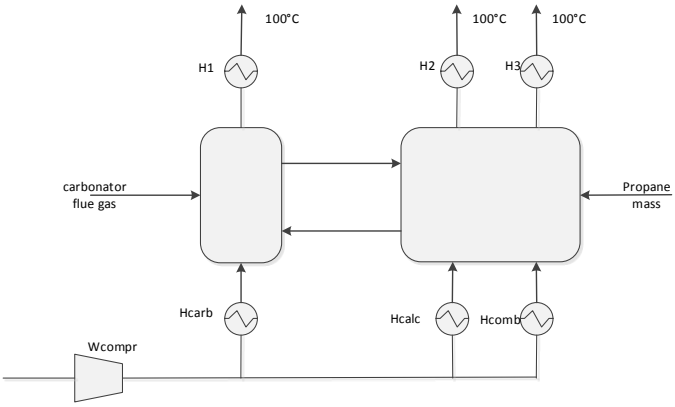

Figure: 29 Diagram of the main sources of energy –Ca looping

$$\sum Heat = \sum_{i=1}^{3} H_i + Q_{carb} + Q_{comb} + H_{carb} + H_{calc} + H_{comb}$$

$$P_{el,auxiliar} = W_{compressor}$$

$$P_{el,gross} = \Sigma Heat \cdot Factor$$

$$P_{el,net} = P_{el,gross} - P_{el,auxiliar}$$

$$P_{th,comb} = \dot{m}_{propane} \cdot LHV_{propane}$$

$$\eta = \frac{P_{el,net}}{P_{th,comb}}$$

Heat recovered from the CO_2 rich stream in the calciner and from the carbonator represent the main energy inputs for the steam cycle.

The energy sources which can be integrated with the steam cycle are the following:

1. Concentrated CO_2 stream that leaves the calciner at around 900ºC which can be cooled down to ~100ºC before being split
2. The energy in the carbonator resulting from the exothermic reaction and the cooling of the solids coming from the calciner at 950ºC. Q-Carb
3. The gas with low CO_2 content leaving the carbonator at 650ºC, which can be cooled down to around 100ºC before being sent to the stack.
4. Even being a small quantity, the solid purge from the calciner at 950ºC which can be cooled down before disposal or use as cement precursor.

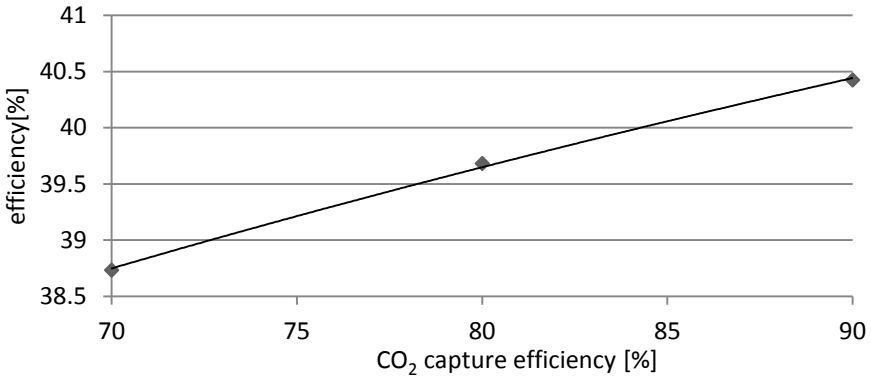

Figure: 30 Efficiency % regarding CO_2 capture efficiency

It can be confirmed that high capture efficiencies are obtained when there is sufficient active CaO in the carbonator per incoming CO_2 flow and this is ensured by a combination of parameters. These include the circulation of CaO between reactors and sorbent make-up flow to maintain sorbent activity what causes a decrease of the solids circulating. Moreover the efficiency of CO_2 capture affects sharply the efficiency and the CO_2 concentration in the outlet of the calciner. With enhanced capture efficiency in the carbonator, the efficiency in the system clearly increases.

5.2.7 Minimum Fluidization in circulating fluidized bed

Previously in chapter 2.1.3 the theory of minimum fluidization velocity has been explained.

According to equation 2.4, a minimum fluidization velocity of 0.036m/s is achieved.

The CO_2 in the reactor is concentrated in the top of it, letting almost free without CO_2 concentration the bottom and the bed of the reactor. Thus, the aim is to achieve a minimum fluidization velocity there where the minimum can take place, in the bed of the reactor. It will be assumed to reach at least the double value of the minimum fluidization recently calculated to achieve a proper fluidization even in the bed of the reactor. For this reason a value of 0.1 m/s as minimum fluidization velocity will be considered.

In this work the fluidization will be performed with air, but could also be that CO_2 mass flow from the outlet gas of the reactor might be re-used to fluidize the reactor avoiding the use of air and the expenses/energy that implies (a compressor to the air, a heating to heat up the air before to entering the calciner). In a recently work has been investigated the potential of fluidize with the CO_2 pure gas released without external fluidization. Self-fluidization can be achieved when the amount of released CO_2 is high enough for fluidize the reactor without the necessity of an external fluidization agent. In it some conditions are determined to let the reactor properly work. [55] The inconvenience in this work with the CO_2 recirculation without air has its base in the equation rates of the reactors. In the carbonator, while the CO_2 concentration increases the velocity in the carbonator increases too, the contrary occurs in the calciner. With recirculating of CO_2 the temperature of the calciner should be increased to have the same effectiveness and to prevent a huge decrease of the velocity. Equation 5.1 and 5.2 For this reason and due to the Carina plant in TU Darmstadt already operating carried out the fluidization with air, in Aspen Plus is going mainly to be fluidized with air.

$$v_{ave,carb} = k_s \cdot S_{ave} \cdot (C_{CO2} - C_{eq,CO2}) \qquad \text{Equation 5.1}$$

$$v_{ave,calc} = k_s \cdot S_{ave} \cdot (C_{eq,CO2} - C_{CO2}) \qquad \text{Equation 5.2}$$

Regarding these equations: v represents the rate reaction, k_s is a constant value characteristic on the sorbent; S_{ave} represents the average reaction surface and C_{CO2} and C_{eqCO2} represent the CO_2 concentration and CO_2 concentration in equilibrium.

The fluidization is strongly dependent on the inlet gas temperature. In this Aspen PLUS model, the air entering the calciner is at a temperature of 500°C. Even so, in the following lines, a calculation according Aspen Plus with a range of temperatures will be performed. It will help to have numerical values when reaching the minimum fluidization.

Because of the higher temperature in the top of the reactor, there the fluidization will be assured if in the inlet –in the bottom of the reactor- fluidization is reached.

To proceed to the calculation of the minimum fluidization velocity with Aspen, some values are needed to perform it which can all be obtained in the simulation.

The pressure is fixed in Aspen Plus with a value of 1.1 bars. As the temperature influences on the density, for each temperature a different value of flow mass will be required to achieve the condition.

In the following table the results obtained by calculation and with Aspen are exposed for different inlet air temperatures.

Table: 5 fluidization values extracted from Aspen PLUS

Temperature inlet air	Molar con-version	Pressure	Density inlet	Minimum inlet flow mass	Density outlet	velocity outlet calciner
[ºC]		[56]	[kg/m3]	[kg/hr]	[kg/m3]	[m/s]
	0.1	1	1.21	123.65	0.35	0.58
20	0.2	1	1.21	123.65	0.35	0.58
	0.3	1	1.21	123.65	0.35	0.57
		1.1	1.33	136.01	0.35	0.61
50		1.1	1.20	123.39	0.35	0.58
100	0.1	1.1	1.044	106.85	0.35	0.53
300		1.1	0.68	69.57	0.37	0.41
		1.1	0.50	51.57	0.38	0.35
	0.2	1.1	0.50	51.57	0.38	0.34
500	0.3	1.1	0.50	51.57	0.38	0.34
	0.1	1	0.46	46.88	0.38	0.34

The values of the last column –velocity outlet of the calciner- are obtained via Aspen PLUS with a carbonation efficiency of 80%. The molar conversion is indicated in the table.

In this table is presented the necessary mass flow rate to obtain a minimum fluidization velocity of 0.1 m/s in the bottom of the reactor depending on the temperature and pressure of this mass flow rate. Furthermore the velocity in the outlet part of the calciner, in the top, is also shown with its correspondent density.

As can be observed, as the air temperature entering the calciner increases, less minimum mass flow inlet is necessary to achieve the minimum fluidization velocity in the bottom of the reactor. The velocity in the reactor depends on the temperature, as higher temperature less density of the fluidization fluid and therefore the mass flow is reduced. The pressure also plays an important role in this fluidization causing a contrary effect than the temperature. With the increase of the pressure the density increases what produces an increase of the minimum inlet mass flow to achieve the 0.1m/s established as minimum fluidization velocity. The molar conversion and the carbonation efficiency also influence in this velocity due to its effect in the circulating solids of the system. Thus, an increase of the molar conversion of the sorbent will produce a decrease of the necessary flow mass entering the calciner –because of the decrease in the solids entering the calciner and therefore less particles to fluidize-.

On the other hand as before mentioned, if in the bottom of the reactor minimum fluidization is assured, this condition will be surely fulfilled in other parts of the reactor. Focusing on the outlet flow rate –last column of the table- the velocity values exceed in all cases the minimum established. This happens due to the high temperature and the lower density because of the mixture with CO_2.

The gas temperature deceases with height because of the heat transfer between the cold particles and hot gas. Near the bottom of column, solid volume fraction is relatively high; therefore, gas temperature decreases rapidly and the rate of decrease is higher for the region near the bottom of the column. At top of the column, there are no particles (gas volume fraction is one) and the wall is adiabatic; therefore the gas temperature is roughly constant. Also the results show that with increasing the gas velocity, as expected the gas temperature decreases. In addition, the gas temperature reaches a constant temperature in the upper region. In the region where the gas volume fraction is highest, the gas temperature is lowest. There is little heat transfer. In the lower part of the reactor the solid volume fraction is higher, so the rate of heat transfer with the cooler particles is higher and the temperature decrease faster.[14]

5.3 Coal model

This study will be divided in two parts; a parametrical study and a study of the concentrations and emissions of the flue gases of the model.

A first part will follow the same steps of parametric study as in the propane model study. The study is going to be performed with Aspen PLUS. Again the main study will be performed varying:

-The molar conversion between 0.1 and 0.3.

-The CO_2 capture efficiency between 70% and 90%.

-Make up flow constant.

The combustor is dependent on the behavior of the calciner since it has to provide the heat necessary to the calciner to achieve complete calcination, but this time the flue gas from the combustor is recirculated to the carbonator what will involve in higher heat demands and circulating solids amounts.

5.3.1 Capture efficiency and molar conversion of the sorbent

RECYCAO is the recirculating solids mass flow coming from the calciner to the carbonator.

RECIRBK is the flue gas mass flow coming from the combustor to the carbonator.

This time the amount of circulating solids has strongly increased compared with the previous model because of the retrofit configuration. There's an addition of CO_2 in the carbonator due to the recirculated gas stream from the combustor redirected to the carbonator. This affects in an increase of the circulating mass flow.

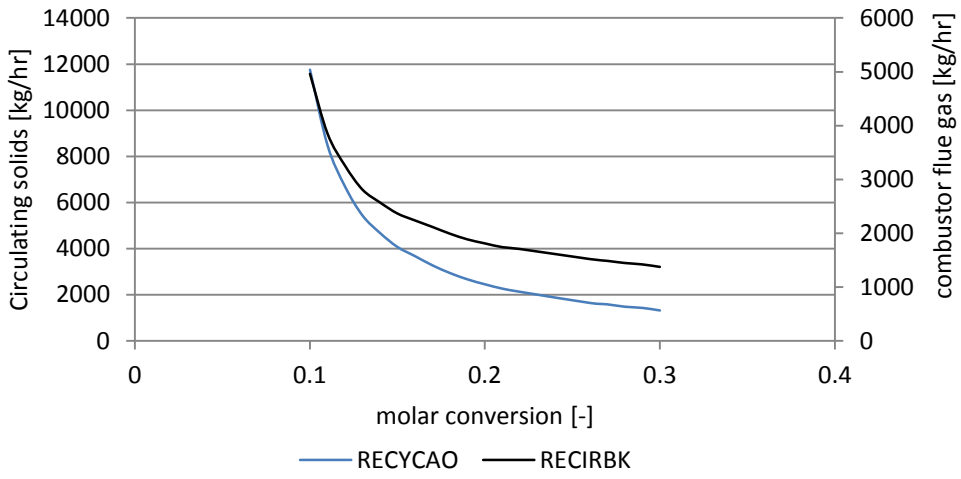

Figure: 31 Molar conversion Vs. recirculated solids and flow gas entering the carbonator. 80% capture

As the limestone make-up added in the carbonator increases the circulating solids flow undergoes two differentiated phases. Notably it has a little influence for the firsts amounts added of make-up flow. Until at one point then it starts to increase quite more prominently.

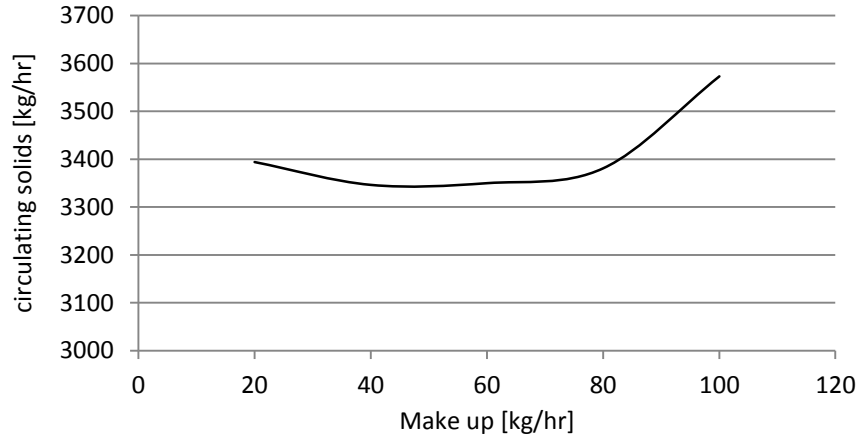

Figure: 32 Mass flow of make-up inserted into the carbonator(kg/hr) Vs. Solids Recirculated to carbonator(kg/hr) Capture efficiency and molar conversion of the sorbent constant.

The limestone added in the carbonator as make up provoke for large amount of make-up flow in general an increase of the circulating solids. This is due to more limestone is calcined giving as product more CaO. At the same time, the increase of material in the calciner implies an increase in the thermal power of combustor what originates more flue gas –containing CO_2- entering the carbonator from the combustor. Thus, the total amount of CO_2 in the rich flue gas from calciner increases, and respectively flue gases in the system increase too.

5.3.2 Carbonator cooling

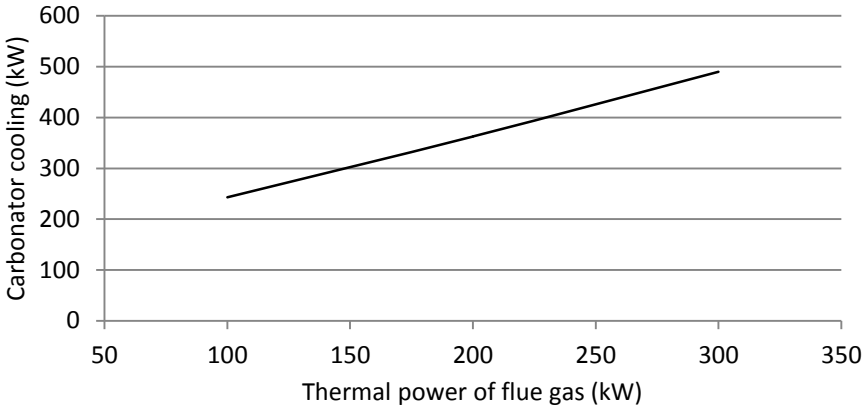

Figure: 33 Carbonator cooling Vs. Thermal power of flue gas

With increasing the thermal power of flue gas, increases the carbonator cooling. This make sense due to when thermal power is increased, the inlet mass flow rate in the carbonator increases too. In the carbonator is not just being recirculated the solids coming from the calciner but also the flue gas coming from combustor – containing CO_2-. The flue gas coming out from the combustor is normally at the highest temperature of the system and contributes in a large increase of the carbonator exchange cooling.

By the other side, with reference to the molar conversion of the sorbent the same pattern as comparing them with circulating solids entering the carbonator is observed. In this case, fewer solids entering the carbonator involve less mass flow amount of high temperatures flow and for that reason, less heat exchanger necessary from the carbonator to cool it down back to 650ºC.

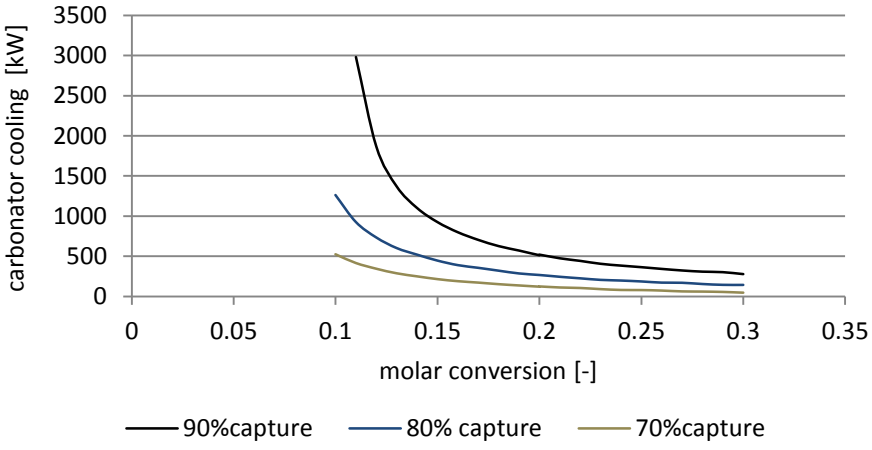

Figure: 34 Molar conversion of the sorbent Vs. Carbonator cooling (kW)

In the graph can be observed how the variation of the molar conversion entails a large variation in the carbonator cooling especially with 90% capture where more amount of circulating solids are involved.
Another point to take into account is the study between the make-up flow and the carbonator cooling. By and large, as make up increases, the carbonator cooling powers tends to increase too. As has been seen before, a large increase of make-up provokes an increase of the solids, which are coming at high temperatures, i.e. more work will be necessary to cool down the carbonator. But in the smaller values of make-up, the carbonator cooling doesn't follow this tendency.

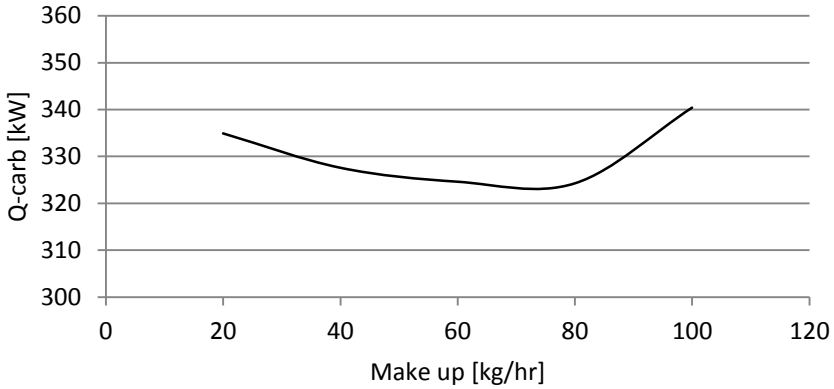

Figure: 35 Carbonator cooling depending on the make-up ($CaCO_3$) flow inserted in the carbonator.

The early adding of make-up, not just flow mass at an ambient temperature is being introduced (makeup flow mass) but less recirculating solids (in small extent) are entering the reactor; in this situation the average temperature of the reactor decreases, for what less work is necessary to cool down the reactor. When the Q-carb increases again, the circulating solids are increasing and the average temperature of the solids entering the carbonator increases together with more mass flow necessary to being cooled down.

5.3.3 Thermal power of combustor and heat pipes power

Regarding to the thermal power of combustor in the following graphs can be observed how an enhancement of the molar conversion of the sorbent involves a lower power thermal of the combustor, following the same pattern as the recirculating solids regarding molar conversion. Furthermore the heat pipes power increase with more carbonation efficiency. This is consistent with the increasing of the circulating solids entering the calciner what causes more necessary heat pipe power.

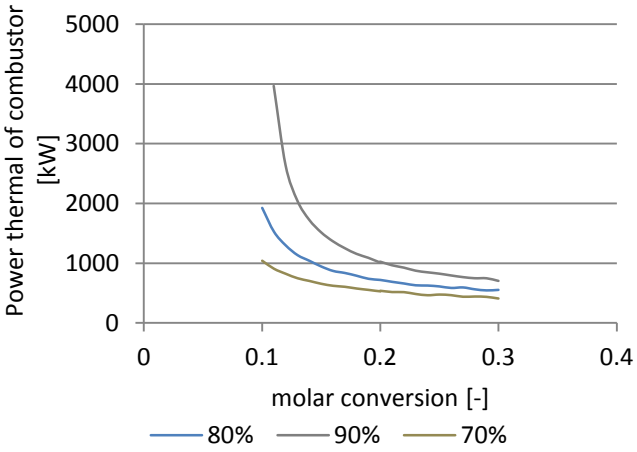

Figure: 36 Thermal power of combustor regarding molar conversion

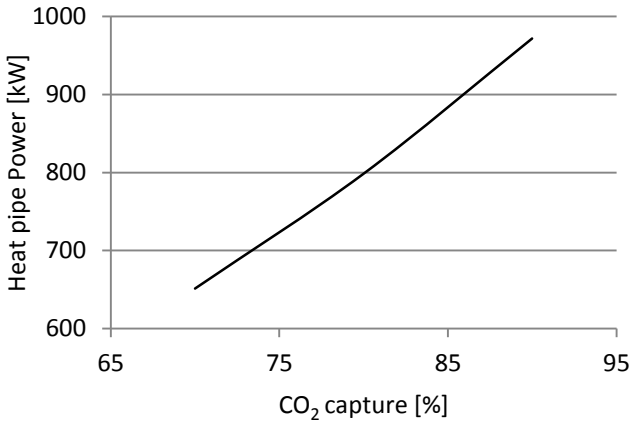

Figure: 37 Het pipe power regarding CO2 capture efficiency

With the increase of molar conversion less heat is necessary to provide to the calciner due to less amount of circulating solids are entering in it. The progress of the circulating solids regarding the development of molar conversion in the sorbent suffers a decline due to improving efficiency of the carrying capacity of the sorbent. Moreover, the increased capture ratio in the carbonator lead to an increased solids mass flow. The effect is an increased heat duty of the calciner due to more CO_2 has to be released. Consequently more coal is burnt in the combustor what involves an increasing amount of CO_2 in the carbonator inlet. This effect converges at high energy requirements. If comparing the values of heat pipes power of thermal power of combustor [kW] result in very high values compared with the case of the model using propane as fuel, in the scale of ten times more.

5.3.4 Composition in coal model

A second part of the analysis consists in the study of main concentrations of some compounds in the solid circulating mass flow such as ash or gypsum and concentrations of the outlet flue gas emissions (such as CO_2 and SO_2). This study will focus more on an environmental study and will help to acquire a trivial knowledge about emissions and harmful components in the system.

This time, new components will be in the system because coal combustion produces a range of compounds that will be redirected to the system/carbonator. The main compounds produced during combustion are CO_2, CO, H_2O, SO_2, N_2 and O_2.

From an environmental perspective, it is going to pay special attention to SO_2, CO and CO_2 which are harmful for the environment and the most controlled by legislation. It is noteworthy that clean coal technologies are used in this system, for what in a good start they allow conditions the most ideals possible to coal combustion.

5.3.4.1 CO_2 concentration in the outlet calciner

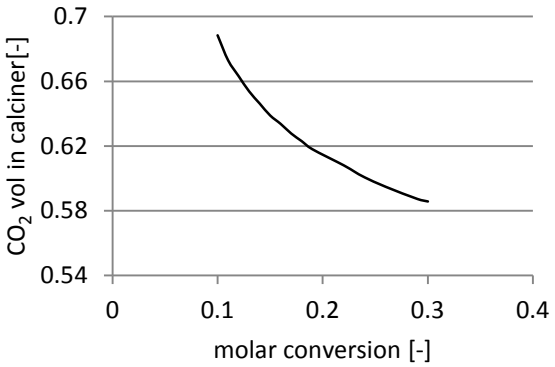

Figure: 38 CO_2 vol% in outlet gas from calciner over molar conversion of the sorbent

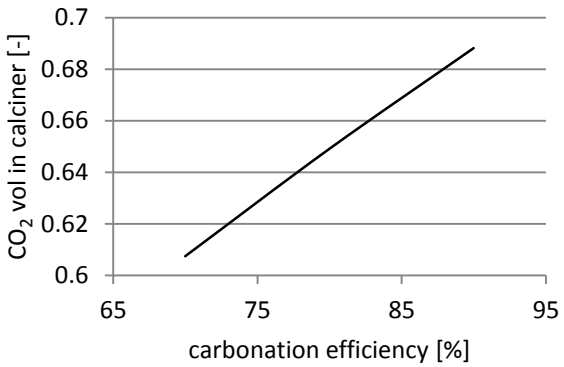

Figure: 39 CO_2 vol% in outlet gas from calciner over carbonation efficiency[%]

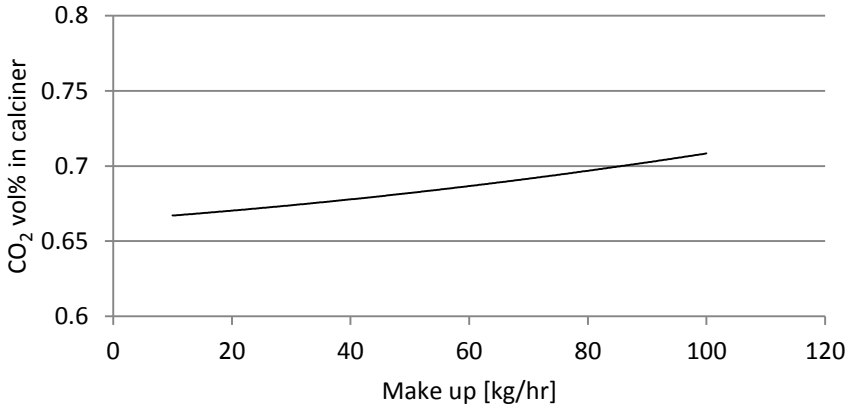

Figure: 40 CO_2 vol in calciner over make up flow

As can be observed in the graphics above, the improvement of molar conversion and capture efficiency have contrary effects. With an enhancement of the sorbent carrying capacity, less circulating solids are necessary in the system to achieve the same carbonation efficiencies. This affects in less limestone entering the calciner producing a lower CO_2 content in the outlet flue gas of the calciner. On the other hand, with the increase of the CO_2 capture efficiency, because of the subsequently increase in circulating solids more CO_2 is produced in the calciner.

Regarding the limestone make up flow an increase of limestone make up flow will produce a direct effect in the CO_2 concentration. For the same values of capture efficiency, CO_2 concentration strongly depends on the $CaCO_3$ make up flow because of the additional CO_2 released during its calcination and the CO_2 released from the additional coal used in the calciner to drive the calcination of the make-up flow.

5.3.4.2 Main composition in exhaust flue gases

To understand the compositions and concentration in the streams within the system is important to have an idea of coal combustion and its main components and products.

Basically, in a practical point of view, coal has four main constituents:

Water (moisture) that indicates all the water wetting the surface or included in the pores which is released heating it at not high temperatures. A second constituent named volatile matter that represents all gaseous species except moisture released by thermal decomposition of the solid. This process is called devolatilization or pyrolysis and it takes places when is heated at high temperatures in an inert atmosphere. Volatile matter is mainly composed of a mixture of hydrocarbons -CO,CO_2,H_2 and H_2O- and in different proportion by other compounds-NH_3,H_2S and CO_2-. The solid residues after devolatilization are known as char and ash. The third constituent is fixed carbon, this is the solid carbon found in the char. Ash is the last constituent, is a non-combustible mineral matter. Ash particles contribute to the establishment of the bed inventory, may be responsible for the release and or capture of gaseous pollutants and may induce bed sintering and agglomeration.[49]

The oxidation of the volatile matter contributes to a significant fraction of the total amount of heat released. After devolatilizations is over, fixed carbon reacts with the gases surrounding the char particle in the bed.

In a oxidizing environment solid carbon react with gaseous oxygen to form CO_2 or CO.

$$C + 0{,}5O_2 = CO \quad AH = -111kJ/mol \rightarrow CO + 0{,}5\,O_2 = CO_2 \qquad \text{Equation 5.3}$$

$$C + O_2 = CO_2 \quad AH = -394kJ/mol \qquad \text{Equation 5.4}$$

Once the oxygen is consumed char combustion occurs in a reducing environment by the gaseous components produced by devolatilization and combustion reactions. The combustion of char is one of the most important reactions taking place inside the combustor and this reaction provides practically all thermal energy need for supply energy to the endothermic reaction of the calciner. As the oxygen concentration increases the devolatilization, as well as ignition, occur more rapidly.

Burning coal is a leading cause of smog, acid rain and toxic air pollution. But the emissions especially NOx and SOx are severely reduced when coal combustion is carried out in circulating fluidized beds. One of the main gas emissions produced by coal combustion is sulfur oxides. The use of calcium-based sorbents produces an in-situ capturing of sulphur oxides emitted during the fluidized bed combustion FBC of solid fuels. The interesting of this process is that limestone achieves high sulphur capture efficiencies around a typical range of FBC operating temperatures ((Lyngfelt and Leckner, 1989; Dam-Johansen and Ostergaard, 1991a, 1991b; Chi et al.1994;

Mattisson and Lyngfelt, 1998a, Anthony and Granatstein, 2001). Morevoer, instead of leaving the reactor as a gaseous pollutant sulfur is discharged as a solid residue.

$$CaO + 0{,}5\,O_2 + SO_2 \rightarrow CaSO_4 \quad \Delta Hr = -116.9\,\frac{kcal}{g \cdot mol}$$ Equation 5.5

This process undergoes two steps: a first calcination of the sorbent that yields a more porous calcium oxide suitable to capture SO_2 and give $CaSO_4$ (gypsum). This reaction is thermodynamically favored under oxidizing conditions in the range of FBC operating temperatures (700-900°C). Nevertheless the importance of the exothermic sulphation reactions is insignificantly and negligible in front of the overall energy balance. [54] Furthermore, this activity of the sorbent in this reaction is considered 99% due to the high Ca/S ratio in the carbonator.

To begin with, a table pointing out the concentrations of each compound of the outlet flue gas of the reactors is presented at a capture efficiency of 80% and 0.2 molar conversion to take a first contact with its compounds and concentrations.

Table: 6 concentrations in outlet flue gas of ca-looping.

	Flue gas rich CO_2	**Flue gas lean CO_2**	**Flue gas outlet combustor**
CO_2	0.8	0.032	0.14
CO	37 PPB	435 PPB	465 PPB
O_2	0.038	0.065	0.033
H_2O		0.074	0.079
NO	34 PPM	245 PPM	261 PPM
NO_2	270 PPB	767 PPB	821 PPB
SO_2	51 PPB	720 PPB	472 PPM
SO_3	3 PPB	6 PPM	7 PPM
N_2	0.162	0.829	0.748
H_2		118 PPB	126 PPB
S			trace
CL_2		trace	trace
HCL		23 PPM	25 PPM

The main concentrations in the flue gas CO_2 rich are remarkably CO_2 and air, leaving in a place far behind other concentrations. By contrast, in the outlet flue gas from the carbonator the main concentrations are SO2 and CO like in combustor.

SO_2 is an emitted gas pollutant formed in the combustor due to the coal combustion reaction. The outlet flue gas from the combustor is directed to the carbonator where most part of this SO_2 takes part to form $CaSO_4$. Equation 5.5. Once formed, the gypsum is directed to the calciner, but the SO_2 and other compounds like SO_3, CO, NO_2 and NO produced in the combustion reaction are filtered in the first cyclone where they leave with the CO_2 lean flue gas. As can be seen in the

Table: 6, the outlet flue gas of the calciner also contains SO_2 and other "impurities gases". According to several studies, have been demonstrated that oxidizing and reducing conditions in a FBC appear to be important regarding the SO_2 capture capacity of the sorbent particles. When sorbent particles which have already captured SO_2 enter into reactor zones lean in oxygen, the calcium sulfate is reduced (in an oxygen deficient zone) thus releasing SO_2 and being converted back to CaO. [57] In this case this is happening on a tiny scale and insignificant SO_2 is released. The same happens with SO_3, since $CaSO_4$ also responds to the equation 5.4. In this way, also in a tiny scale, the calciner may also releases SO_3.

$$CaO + SO_3 \longrightarrow CaSO_4$$ Equation 5.6

NOX: Nitrogen oxide emissions

Coal combustion generates nitrogen oxide emissions, what contributes significantly to ozone decomposition and acid rain, and might react with volatile organic compounds to form photo-chemical smog*.The main three nitrogen oxide species emitted from fluidized bed combustors are nitric oxide (NO), nitrogen dioxide (NO_2) and nitrous oxide (N_2O). The first two called NOx. These emissions are mainly dependent on the nitrogen content in the fuel used. [21] As absorber of infrared radiation N_2O is more powerful than CO_2, and its emissions are much higher in fluidized beds than in other combustion systems. In this work are not going to be considered. [14]

Regarding molar conversion of the sorbent, the main compounds in the analyzed streams are depicted in the following graphs.

* Photochemical smog is the chemical reaction of sunlight, nitrogen oxides and volatile organic compounds in the atmosphere, which leaves airborne particles and ground-level ozone.

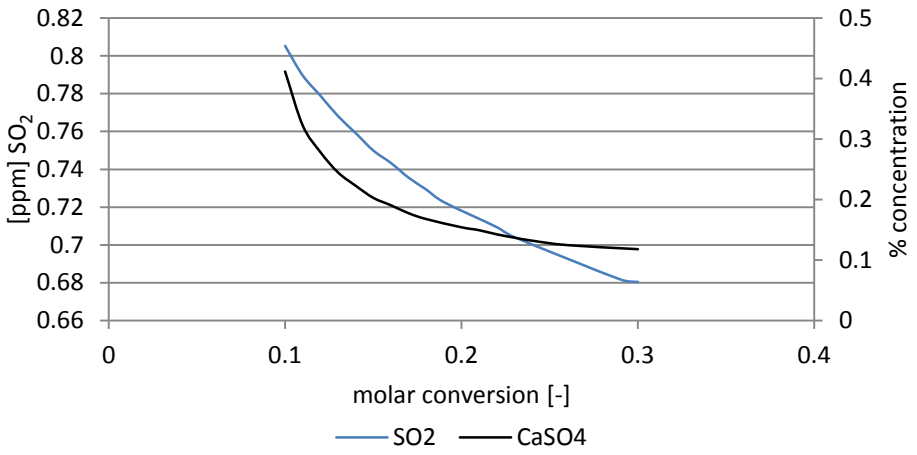

Figure: 41 Concentration of $CaSO_4$ and SO_2 going out the carbonator 80 % CO_2 capture

In this graph is depcited the molar conversion regarding the SO_2 and $CaSO_4$ concentration going out from the carbonator. As can be seen, both concentrations decrease with the improvement of the molar conversion. Because of the lowering in the activity of the sorbent, a further decrease in the circulating solids is produced. The make up flow this time is a fix value for what the decrease in $CaSO_4$ concentration is obvious. On the other hand less SO_2 is entering in the carbonator, because less heat demand is necessary for what less coal is burnt in the combustor.

At the same time, increasing the CO_2 capture increases the required solids circulating, what will increase the product of $CaSO_4$. By the other side, an increase in the capture efficiency will lead to a higher concentration in SO_2 in the outlet of the calciner.See Figure: 42

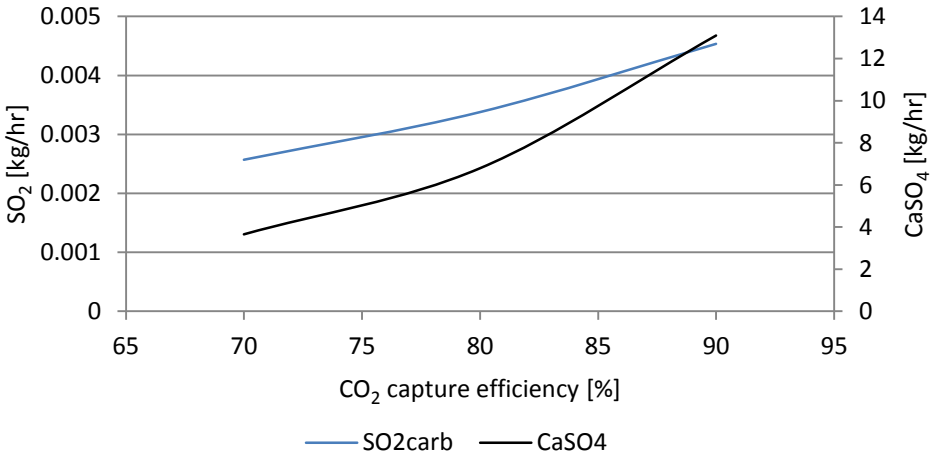

Figure: 42 Flow mass of SO_2 and $CaSO_4$ in the carbonator along different efficiencies of CO_2 capture.

5.3.4.3 Concentrations in the two filters: PURGE and ASH

Another part of this chapter consists in analyze the concentration going out from two purge outlet solids varying some parameters to see its concentration changes. In this model there are two purge outlets. The first one is called PURGE. It is situated between the two reactors carbonator and calciner, after the first cyclone. This filter is the responsible to regulate the amount of circulating solids within the system so the purge PURGE mainly consists of CaO, $CaSO_4$, $CaCO_3$ and Ash. It is a method to prevent ash and deactivated sorbent accumulation in the system. This coal ash and spent sorbent can be problematic to landfill but there are interesting alternative application fields for theses wastes such as their re-use in the low energy cement industry –the spent sorbent purged in this process can be used in the cement industry as raw material for clinker manufacture- and the reactivation by hydration of their desulfurizing ability.

The second solids purge is called ASH and is situated in the way from the combustor to the carbonator. Its aim is to allow only a specific value of SO_2 amount to achieve the carbonator. All the rest is deposited through the filter. For this reason, the solids concentration leaving the filter will be purely of SO_2.

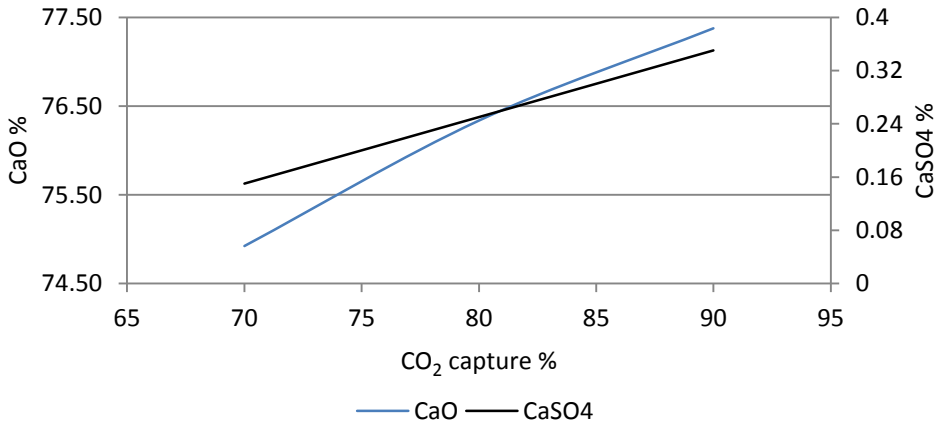

Figure: 43 $CaSO_4$ concentration % and CaO % in the outlet of the PURGE filter [ppm] along % CO_2 capture. 0.2 molar conversion

As the CO_2 capture increases, the concentration in the circulating solids of $CaSO_4$ increases too, because an increase of the solid circulating is provoke. The same happens with the concentration in CaO of the total solids. An increase of the capture efficiency in the carbonator increases solids circulating on the system. Because of the value fixed of make-up, the limestone composition in the purge decrease, whereas the other composition, CaO and $CaSO_4$ win weight.

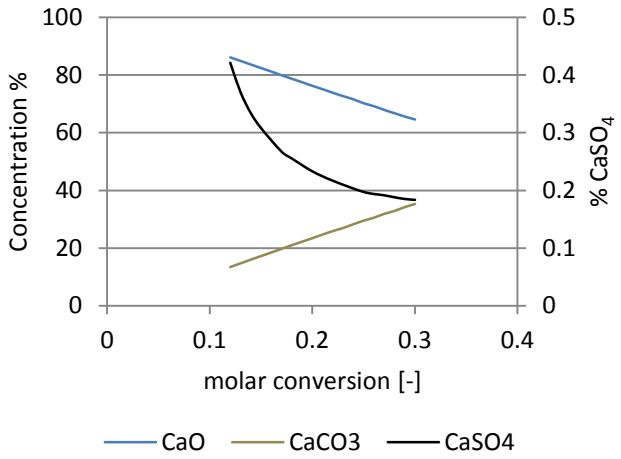

Figure: 44 PURGE concentration along molar conversion

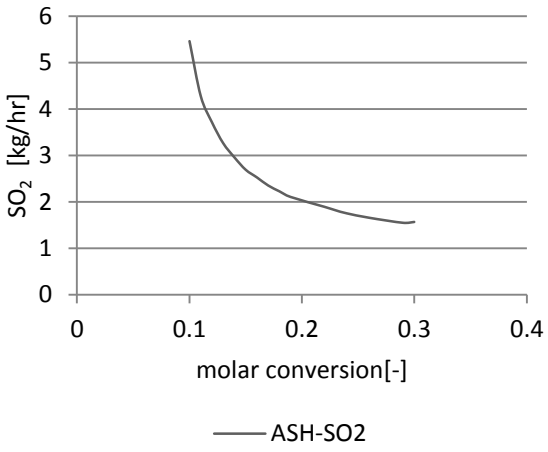

Figure: 45 SO_2 [kg/hr] along molar conversion

As the molar conversion increases, the $CaSO_4$ going out from the filter PURGE will follow the same pattern than the circulating solids mass flow over the same parame-

ter. Contrary the limestone concentration increases as the

molar conversion increases. This is due to the fact that along the increase of the molar conversion, fewer solids are in the system and due to the limestone make up remains constant, the concentration will be balanced in its favor.

The Ash purge is purely composed of Ash and its flow mass (SO_2) will decrease also at the same rhythm than compounds in combustor decrease with the lowering of the activity of the sorbent .

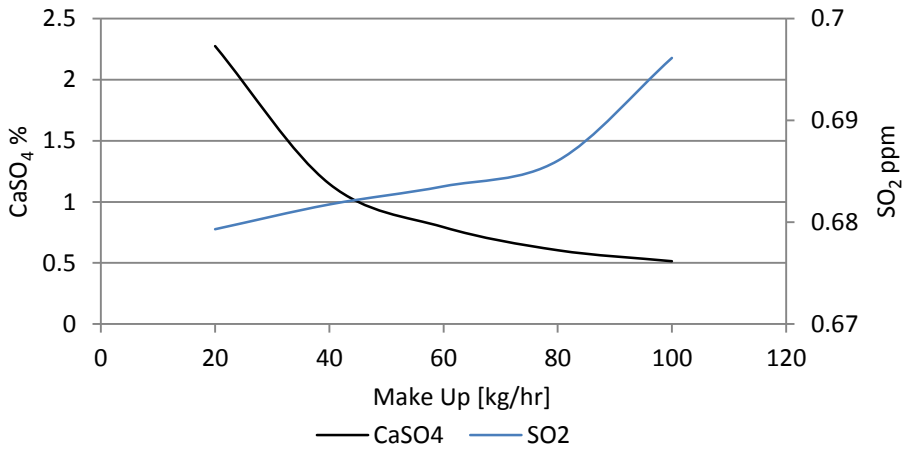

Figure: 46 $CaSO_4$ % and SO_2 concentration [ppm] through an increase of the make-up flow.

As is normal, once the $CaCO_3$ Make up starts to increase to be added in the carbonator, the concentration of $CaSO_4$ starts to decrease. The limestone is winning concentration. Furthermore, the increase of SO_2, is due to the increase heat demand produced for the increase of limestone make up flow.

The concentration of SO_2 in the calciner , being in an order of 10times lower, follows the same line as in the carbonator. Contrary, the concentration in combustor remain constant with high values.

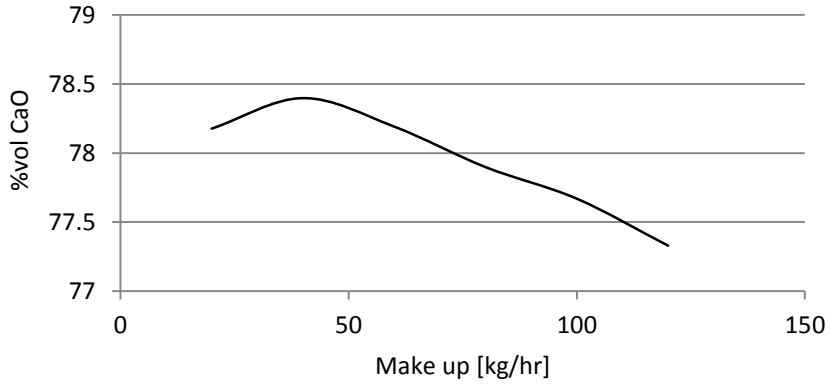

Figure: 47 Concentration of $CaSO_4$ and CaO in the PURG filter when increasing make up.

As the make up increases, the concentration of both decreases because more limestone is taken part in this concentration. About quicklime as $CaSO_4$ concentrations decreases and limestone concentration increases with the adding of more make up, the result of the CaO concentration is the shown in the graphic.

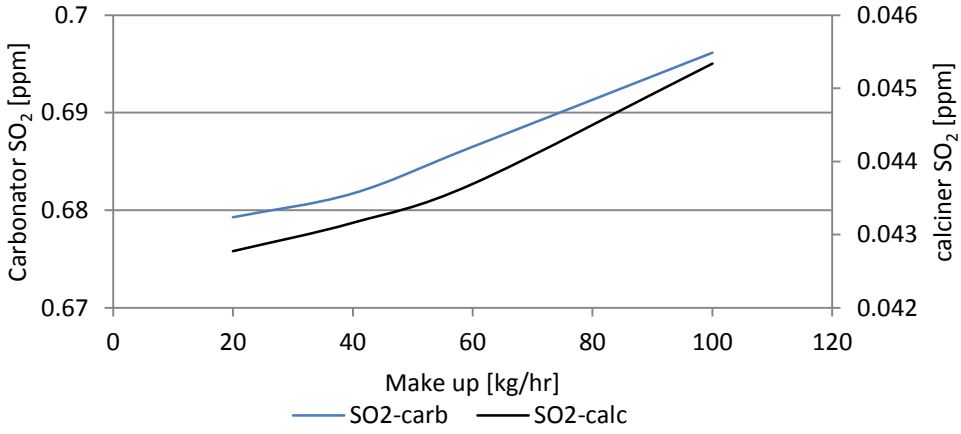

Figure: 48 SO_2 concentration [ppm] with increase in make-up flow

In this graphic is depicted the SO_2 concentration in calciner and carbonator over an increase of the make-up amount. It increases the same way as circulating solids increasing under the same conditions. The SO_2 concentration in combustor is constant and much higher than these amounts, around 10000 ppm.

6 Analysis of 300kW$_{th}$ pilot plant measurements

This chapter deals with the analysis of the data collected during the performance of Carina plant in from (the period of days from) the 10.02.2015 until 14.02.2015.

One of the main objectives of this chapter is the comparison or contrast of the data got from the plant with the results obtained in the program Aspen Plus. One of the most extensive task in this work has been to perform a model with Aspen Plus that represents in the most loyal way the Carina Plant build up and put in operation in the beginning of February in the University of Darmstadt TU Darmstadt. The aim of this chapter consists in a first analysis of some parameters and a further comparison between the data obtained and the results obtained with Aspen PLUS. Its aim is to evaluate approximately the error that the program Aspen Plus gives when reading its results. An idea of with how much reliability can be read the data obtained from Aspen and what possibility of error exist with what even existing these errors between reality and simulation, may be achieved an approximate idea of numeric values for further operating of the plant.

6.1 Method of performing

After 5 days being the Carina Plant operating and taking data at every second, an exorbitant data base with all characteristic of the desired parameters is in our possession to be studied. For this reason, the previous step has consisted in carry out an average every 10minuts, thus reducing and making more affordable data handling.

The first step performed in this chapter has been to obtain the CO_2 capture efficiency in the carbonator in each instant. Is an essential step to recognize with what effectiveness does the carbonator executes its work. Other parameters of the system are also analyzed such as temperatures of the reactors along time, the continuity in the air flows or combustible flow entering the combustor and other reactors or such as outlet flue gas composition of the reactors.

To carry out a comparative study between the program Aspen PLUS and the data obtained from the plant operating there are two important data that are unknown. These data are the molar conversion of the sorbent and the circulating solids which couldn't be accurately calculated. As difficulty, without the reliable assumption of one of these two parameters, the model with Aspen PLUS will not be able to simulate in a proper way the system -or at least trying to get closer results to the reality-. Thus, thanks to a resource with the L-valve -see Figure: 11 SSPLIT-, the value of the circulating solids within the system can be approximate, having subsequently as unknown just the molar conversion of the sorbent. The action undertaken with the valve has been only carried out within a specific time instants, for what an after stability study of the parameters has to be

performed in that instants of time to determine if the study in that instant is effective. Otherwise, there's a possibility that the pressure in the L-valve hasn't changed over time, what means –if other inlet parameters are on the order of stable, a similar solid circulation- and then a suitable instant of time might be found to carry out the analyze. Another issue is to give with the proper fraction amount of solids that are circulating to the calciner-and subsequently the fraction of solids circulating back to the carbonator-. Information that can help is the temperatures of both the L-cone valve and the T looping seal. If these two temperatures have huge differences, this means that the solids are going through the one with more temperature. By contrast, if they are similar, this indicates that in both ways are solids circulating. It cannot exactly known the amount of solids circulating in each way, but with the temperature information and comparing pressure values, an approximate idea can be acquired through these two steps.

The fact of looking at the stability of the parameters is necessary to carry out a study the most reliable possible.

6.2 Data analysis of parameters

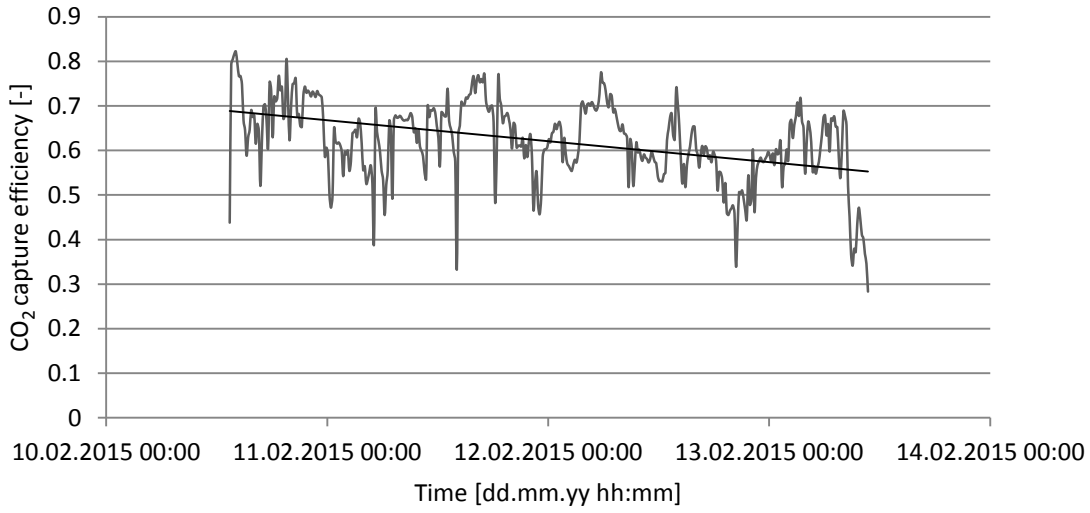

Figure: 49 CO_2 capture efficiency over time

The early data of the test campaign regarding CO_2 capture efficiency has been disregarded because they involved flamboyant "turbulences" due to the starting of the plant. The same has been considered in the last instants of the operating plant when the shutting down was carried out. Furthermore in database a point that was beyond the limits altering significantly the graph and values has been ignored considering it as non-significant and excluding it of the database. In its stead linearization has been carried out to approximate a value -although the graph doesn't follow a linear pattern, it was not desirable an empty point in the graph-.

The CO_2 capture in this period of time is shown quite unstable and decreasing over the days. In many periods of time the values are located above 70% reaching in some occasions 80% -mostly in the begging-.

In the following graph is shown how is changing the temperature in each reactor according to their height. To perform this graph has been chosen a range of time where CO_2 capture remains stable. The chosen period is between 11.02.2015 at 8:14h until the same day at 08:44h. The stability of other parameters such as inlet mass flow in reactors has also been analyzed during this period of time.

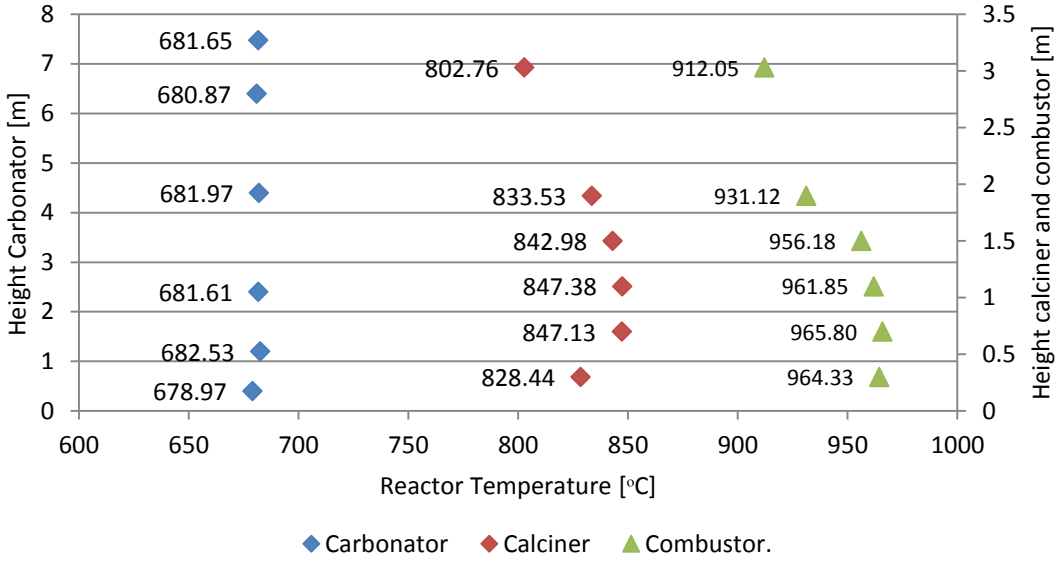

Figure: 50 Temperature of reactor according different height of each.

Because of in this first operating the carbonator did not has a cool exchanger built-in to keep the temperature at 650°C, the reactor wins temperature every day.

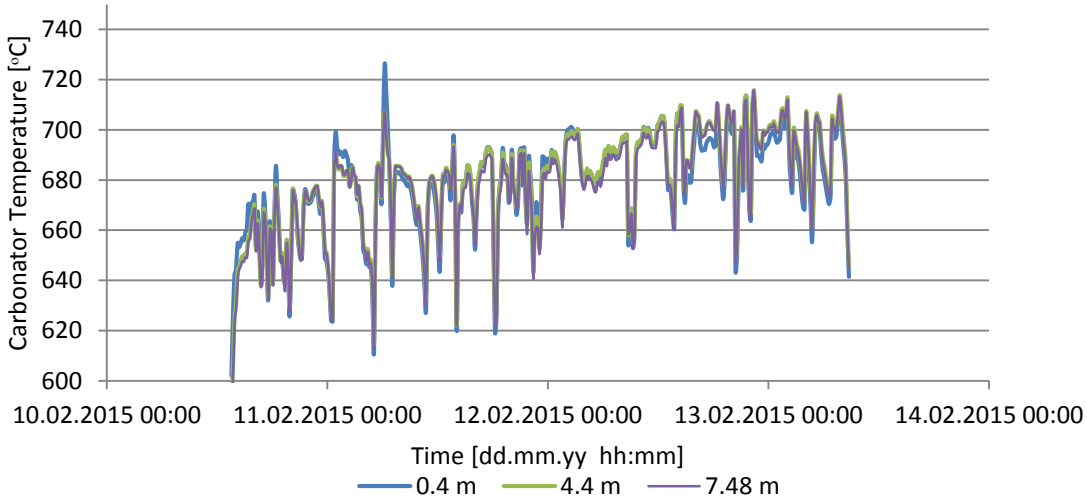

Figure: 51 Carbonator temperature [°C] over time [min]

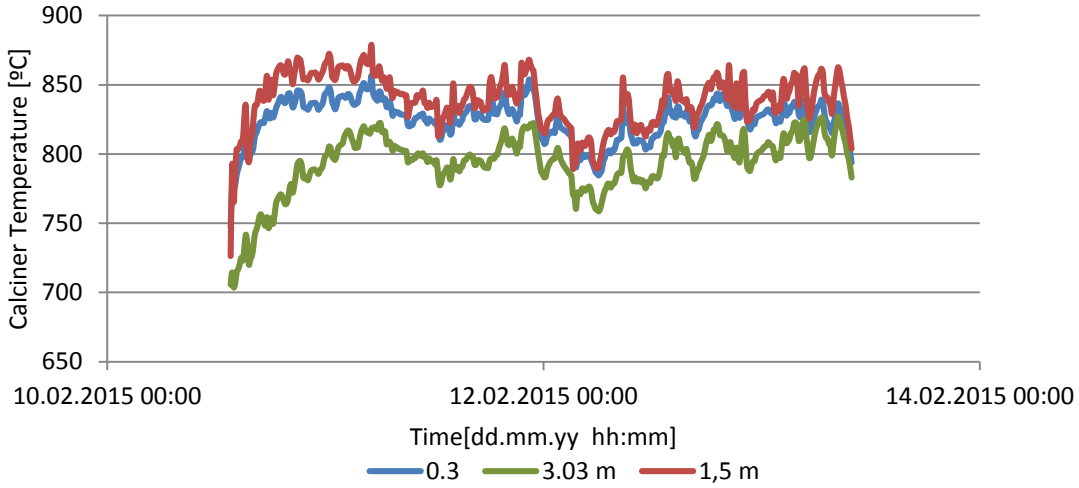

Figure: 52 Calciner Temperature [°C] over time [min]

The temperature of the calciner is kept within quite stable limits. In the core of the reactors is where more temperature is acquired and in the bottom and on the top where the outlet gases loses temperature. In this reactor, the highest temperature is found where the bed is formed. There is where major particles are gathered and where the temperature is higher. The intern temperature can be indirectly varied through the adjustment of the inlet air flow and circulating solids entering the calciner.

The temperature in the calciner should be as high as necessary to make sure that low content of $CaCO_3$ is leaving the calciner in the solids. Nevertheless it is also known that the heating of the inert solids flowing from the carbonator to the calciner contribute to the heat demand in calciner, and for that reason the energy consumption will increase in the calciner as temperature in the reactor increases. [54]

In the combustor, the temperature is presented more instable and wins temperature with the height. Temperature distribution in combustion chamber is nonlinear in character. [58]

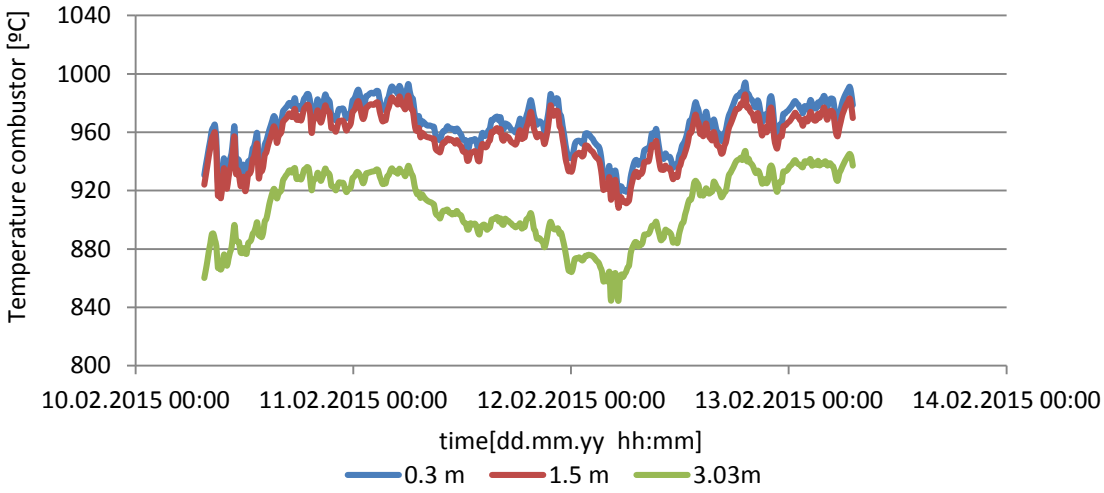

Figure: 53 Combustor temperature [°C] over time [min]

Combustion of coal and main characteristic in fluidized circulating beds

In coal-fired bed combustor there are various solids types, e.g. coal fuel, char, ash particles and additional inert material. The reactor where the coal combustion takes place is named combustor. It has a dense bed in the bottom and there is a vertical distribution of solids.

The fuel fed into the combustion chamber and when heated, the organic matter of coal is pyrolyzed evolving as volatile. So devolatilizes and undergoes a mixture of carbon and mineral matter, which is referred to as char. The ash remained after the char is burned off. The combustion of char, in its simplest form, is assumed to produce a mixture of CO and CO_2:

$$C + O_2 \rightarrow CO_2 + 394 \frac{kJ}{mol} \qquad \text{Equation 6.1}$$

The fresh coal in the bed surface is heated rapidly, the burning coal then descends through the reducing region and the oxidation region becoming ash. The bed layer where the oxidizing reaction takes place is the highest temperature zone in the bed as can be seen in Figure: 53. [59]

Solids inventory

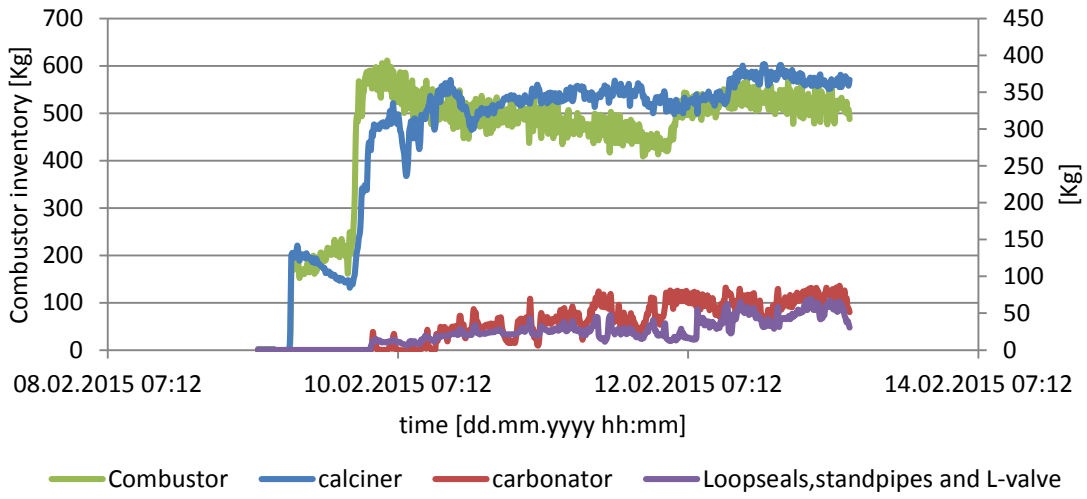

Figure: 54 Solid inventory in system

Clearly the solid inventory in the combustor and calciner are the highest inventory in the system. Contrary because of the smallest area -10 times less than the other reactors- in the carbonator takes place the lowest solid inventory.

The solid circulation and the inventory of the reactor play an important role to define the carbonation efficiency. The flue gas that enters in the carbonator containing CO_2 will react with the active CaO present in the bed inventory.

The efficiency can be described as:

$$carbonation\ efficiency = \frac{CO_2\ reacting\ with\ CaO\ in\ the\ bed}{CO2\ entering\ the\ bed\ in\ the\ flue\ gas} \qquad \text{Equation 6.2}$$

The bed inventory is assumed to contain three types of sorbent particles: (1) an active fraction of CaO reacting in fast regime, (2) an inactive fraction of CaO from earlier carbonation-calcination cycles and (3) a fraction of $CaCO_3$ as results from the carbonation conversion. [56]

The inventory of solids in the fluidized beds is determined through the measurement of the pressure drop between the bottom and the exit of the reactor. The total inventory of solids in the system can be estimated sufficiently accurately using pressure measurements. [60]

In the following graphic the curves of carbonation efficiency and solid inventory in the carbonator are depicted over the operating time of the plant.

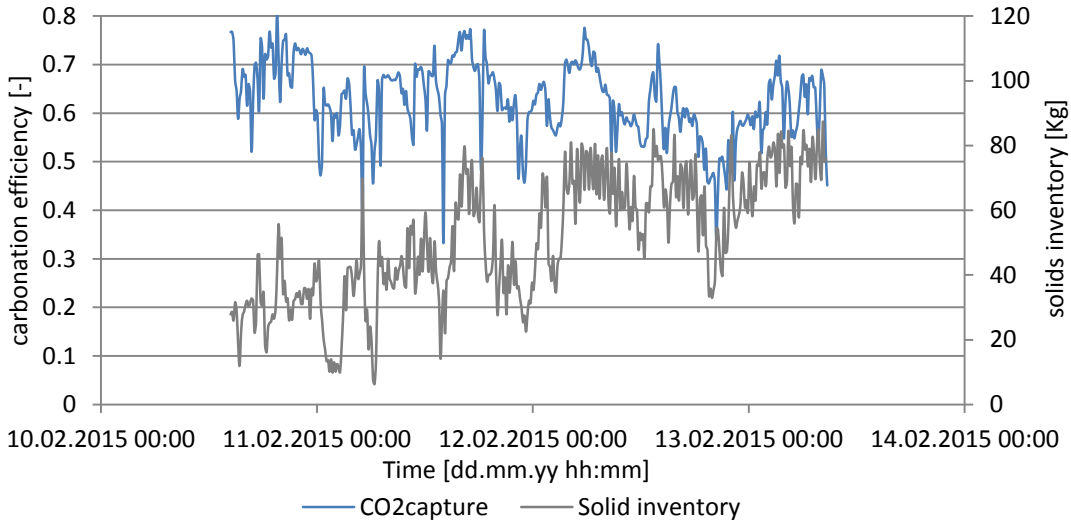

Figure: 55 Carbonation efficiency and solids inventory [kg] mass in carbonator over time

Sufficient amount of active CaO is required in the carbonator in order to achieve high CO_2 capture efficiencies. The necessary amount of active CaO can be achieved by increasing the carrying capacity of the sorbent. According to many studies, the same objective can be achieved by increasing the bed inventory. It is necessary, but not sufficient, that a recycled stream of solids with enough active CaO enters the carbonator to react with CO_2 flue gas entering. When this condition is fulfilled: as it is known low carrying capacity of CaO involves high cycled CaO particles. These ones can then be counterbalanced by enough large inventories of solids in the bed reactor that at the same time by increasing the average residence time of particles can increase the CO_2 carbonation efficiency. [61]

As can be observed they follow the same pattern, when the solid inventory decreases the carbonation efficiency most of times decreases too. According to [62] was determined that one of the most outstanding parameter in the carbonator is the inventory of solids in the bed together with the average activity of the solids in it. This time, solid inventory seems to play an important role regarding carbonation efficiency.

The make-up flow added into the calciner during the functioning time has been varied certain times.

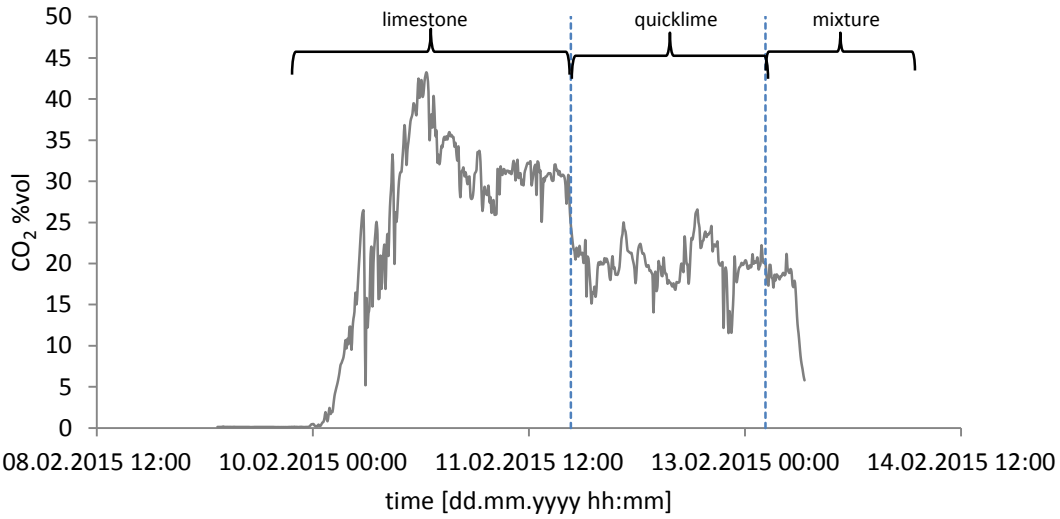

Figure: 56 CO_2 vol % in calciner over time

The make-up is added into the calciner. The advantage of this is that the make-up quicklime doesn't need to be calcined what effects in a lower heat energy demand of the calciner.

In the graphic is showed how the change of limestone make up to quicklime make up produces a considerable decrease in the CO_2 concentration of the outlet gas of the calciner. The limestone as make up provokes a high increase in this result because of more limestone is entering the calciner and subsequently being calcined producing more CO_2. This fact increases the heat demand of the calciner altering all parameters in it.

6.3 Analyzing results with Aspen Plus

To represent in the best way the Carina Plant, the model with Aspen PLUS retains the same structure but some aspects have been varied regarding previous models with which have been carried out previous analyses.

To begin with, as the built up plant has lots of temperature measurements, to adjust more the model in Aspen PLUS to reality, heat pumps have been added to fix the streams at these temperatures.

An essential device for proper operation and the correct configuration of the system/circulating fluidized bed is the L-valve added after the cyclone which allows the rerouting of the solid stream, having the possibility to be directed back to the carbonator or to the calciner. L-valves are non mechanical valves and they are used

extensively in circulating fluidized bed to control solid flow rate. [56] L-valve pressure drop increase with increasing aeration (i.e. increasing solids flow rate), this fact will help to calculate approximately the solid circulation of the system. Furthermore, non-mechanical valves (i.e. L-Valves) have an advantage with respect to mechanical valves; they can be easily adapted to high temperature conditions, thing that meets the requirements of circulating fluidized beds.[60]

The make-up is added now into the calciner. The early days limestone was added as make up but it was changed rapidly to quicklime because not so high values are pursued regarding the CO_2 volume concentration in the calciner. This change of make-up composition entails consequences that will be later analyzed.

Since in this instance we already have almost all necessary data to set the model, most of the design specs have been removed. The only design spec that must remain is the one called HEAT whose function is to achieve that the calciner doesn't need any other external heat source than the given by the heat pipes coming from the combustor. It consists of varying the duty of the combustor in order to get the necessary and enough heat transfer by means of heat pipes to be the necessary in every moment.

The CO_2 concentration in the outlet of the carbonator is also a data, so one of the new specifications will be to force this value in order to fix the CO_2 capture. The molar conversion of the sorbent is unknown, neither the solid circulating within the system, it will be necessary fix properly one of these two values to obtain the other.

6.3.1 Calculation of solid circulation

In the following section is explained in detail how the value of circulating solid is obtained.

The amount of circulating solids with the system even though hasn't been measured can be approximated through actions performed over the L-valve during the operating days in specific instants. A solid flow rate measurement is carried out using batch solid flow between the reactors. The procedure is executed in a very short instant of time – a few seconds- . The solids fall from the cyclone through a vertical standpipe and to a loop seal. Aeration to the second L-valve is closed/stopped causing no circulation of solids to the calciner, but all directed to the carbonator. This causes a pressure drop in the L-valve and after a short period of time the second L-valve is opened allowing the through pass of solids again, going the pressure back to its normal values. The instantaneous solid flow rate is determined using the slope of the curve representing the variation of the pressure drop along the fluidized bed in terms of time as:

$$\frac{dM}{dt} = \frac{A}{g} \cdot \frac{dP}{dt} \qquad \text{Equation 6.3}$$

The following picture reflects this action in the valves during an Δt it causes a pressure drop of ΔP.

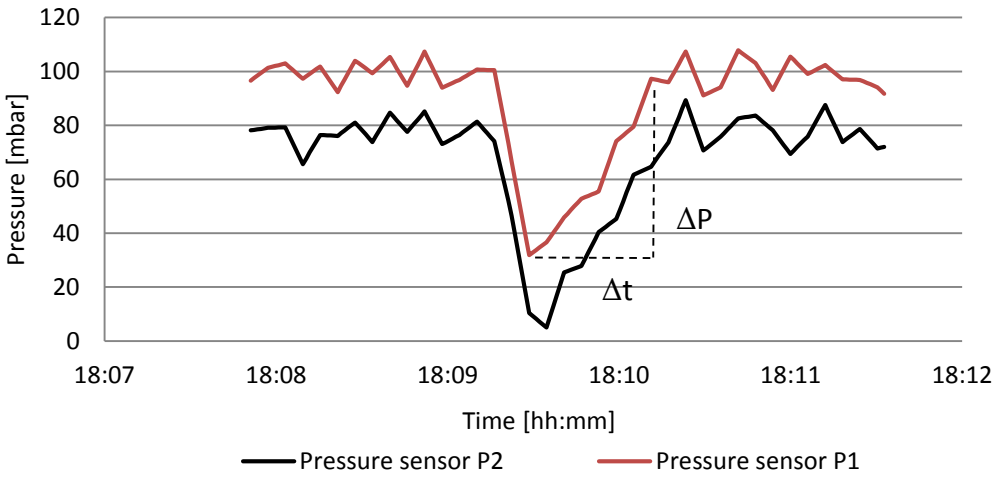

Figure: 57 pressure drop caused by the L-valve action

It is important to note at this point if the parameters are stable. The CO_2 capture is an important result to examine, also the propane mass, the air combustor and inlet flow airs entering the others reactors.

So, before comparing the data with the simulation in Aspen Plus, the stability in these points must be verified.

6.3.2 Time points analyzed

Table: 7 Chosen Points to perform the comparison

Day [dd.mm.yyyy]	Time [hh:mm]	Stability [Yes/No]	Circulating solids [kg/hr]
11.02.2015	14:09	No	670
	15:54	Yes	-
12.02.2015	06:27	No	380
	04:04	Yes	-
	03:44	Yes	-
12.02.2015	18:20	Yes	840
	18:04	Yes	-
13.02.2015	01:34	No	940
	00:34	Yes	-
13.02.2015	07:34	Yes	800-1000

In the following graph- Figure: 58 - showing the CO_2 capture stability the chosen points are marked; in red the non-stable points and in green the stables. The non-stable points have been chosen for the calculation of the circulating solids but they are useless to proceed to the comparison between Aspen PLUS and the data ex-

tracted from the Carina Plant. It is necessary a minimum of stability. This stability is found in the green points. In the stable points marked in the illustration not only are stable regarding carbonation efficiency but also all other parameters.

There exists different possibilities to be able to assume if the circulating solids in different instants of time –but enough close in time- are similar.

The necessity of this comes due to most of the points in which the circulating solids have been calculated are unestable. For this reason different points, closer to the non stable, which present more stability, regarding not only CO_2 capture but also other parameters, have been chosed. The further step is to corroborate if the circulating solids can be assumed similar in the new time point to a proper analyze of the results with the Aspen PLUS software. The pressure drop in the L-valve plays an important role to figure it out. If this value doesn't change considerably during the analyzed points, and inlet parameters are not significantly varying, a similar circulation of solids can be assumed. Anyway, in all cases studied results are going to be proved with different solid circualtion values.

Furthermore important data to keep in mind when analyzing results are the pressure drop in the L-valve and the difference between temperature in the loop seal from the carbonator and the L-cone valve.

With this data, analyzing the pressure value in each interested instant and with the temperature information in the two streams; one going to the calciner and the other recirculated back to the carbonator, a basic idea of the fraction of total solids circulating in each way can be done. These information will help to limit the especifications of solid circulating fraction going to the calciner.

The results are presented in Table: 8.

6.3.3 Comparison of results

Once the suitable –stable- time points has been chosen, an analysis of each one separately has been carried out. Due to the uncertainty of some important parameters, to establish the model in the program correctly, several simulations have been performed varying variables considered uncertain with the aim to get closer and optimal result. Thus, in Table: 8 are presented the main variations carried out in each time point. In grey are represented the values that has been considered in a beginning with all the correspondent assumptions explained before –following the resuts obtained or interpreted fom the data plant-. As can be observed, the parameter that has been most been varied has been the fraction of solids directed to the calciner. Through this variation huge differences are achieved in the results. The reason is that knowledge of this value is just a result constructed from assumptions with temperature of the Loop seal and L-valve and its respective pressure, as we explained before, so the value can vary in a wide range. Moreover, the amount of

circulating solids in the system has also been varied. Still having an initial idea, because of being an estimate value, has to be varied to ensure results. Finally make up mass flow is varied in most of cases due being in some cases rather imprecise. It is varied in a small range. It must be kept in mind that the results are trying to copy the reality -as nearly as possible- to the fullest extent, the closer results to data have been found thus decreasing the error, but the uncertain knowledge about some data let the results quite open.

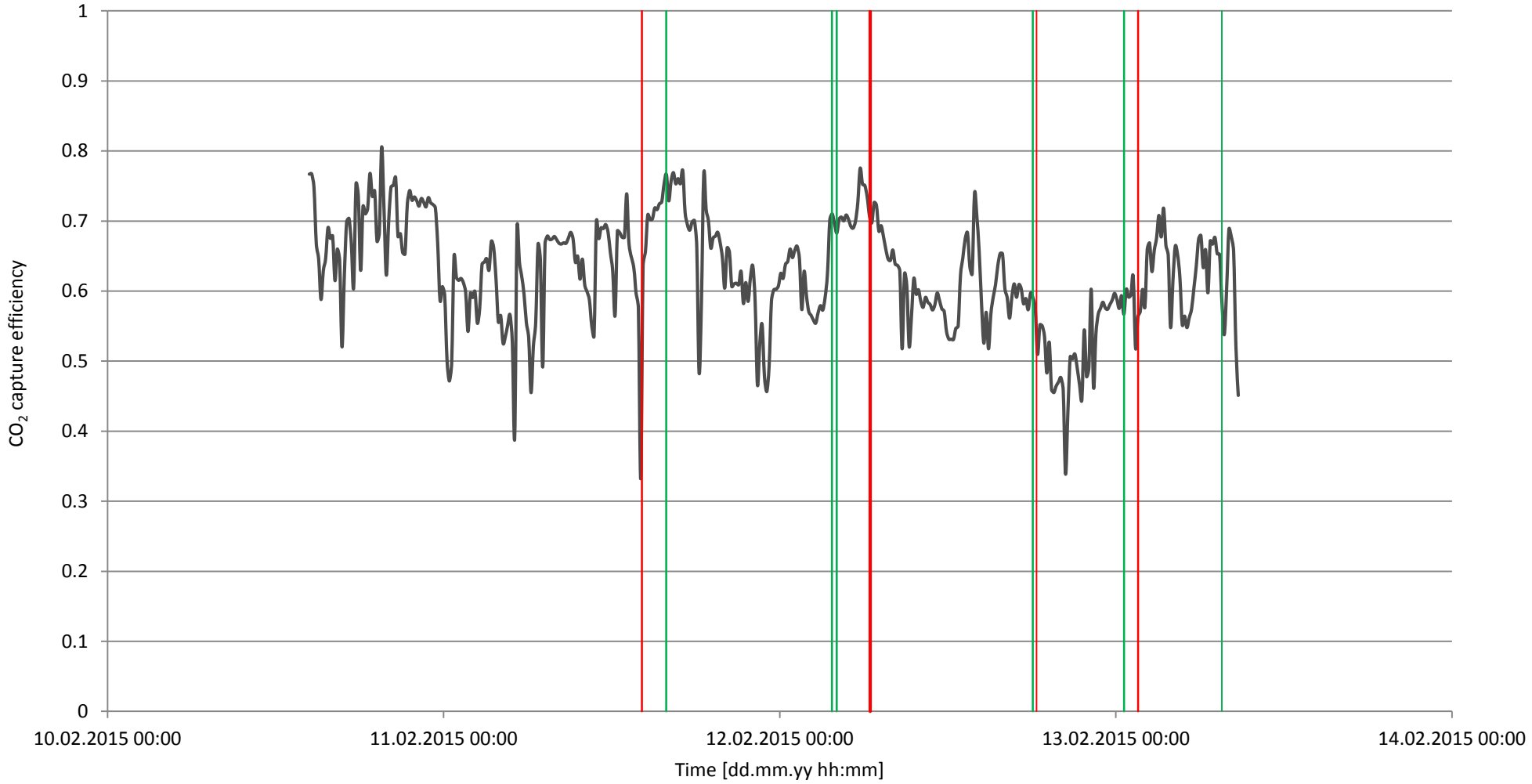

Figure: 58 Chosen points over the CO_2 capture efficiency

Table: 8 Presentation of results

Day	Time	Circulating solids	Fraction of solids to calciner	Make up	Molar conversion	Calciner Flue gas analysis CO_2	Error
dd.mm.yyyy	hh:mm	kg/hr	%	CaO Kg/hr	[-]	%	%
12.02.2015	04:04	380	High		-	23.88	
		450	99	25	0.10	21.41	10.36
		400		32	0.12	20.98	12.15
		450			0.10	21.14	11.48
		380			0.12	20.90	12.51
	03:44	380	High		-	25.01	
		380	90	25	0.13	21.14	15.47
		450	99		0.10	21.47	14.16
		800			0.06	21.92	12.36
		380			0.12	21.27	14.96
	18:24	840	10-15		-	24.50	
		840	30	24	0.08	22.54	8.00
			15		0.13	20.49	16.39
			50		0.07	23.33	4.78
			70		0.07	23.65	3.496
			80		0.06	23.75	3.09
		900	70		0.06	23.71	3.22
	18:04	840	10-15		-	23.77	
		840	15	24	0.17	23.02	3.16
			18		0.14	23.83	0.26
			40		0.09	25.97	9.26
		750			0.10	25.77	8.40
				28	0.10	25.52	7.33
			65	30	0.09	26.22	10.28

Day dd.mm.yyyy	Time hh:mm	Circulating solids kg/hr	Fraction of solids to calciner %	Make up CaO kg/hr	Molar Conversion [-]	Calciner Flue gas analysis CO_2 %	Error %
11.02.2015	15:54	670	10-15		-	30.05	
		670	15	55	0.15	30.13	0.27
			25	50	0.11	31.20	3.81
			35		0.10	31.93	6.25
				45	0.09	31.63	5.24
		650	25		0.12	30.38	1.08
13.02.2015	00:34	940	11		-	19.37	
		940	11	25	0.13	19.46	0.46
		900	15		0.11	20.69	6.81
		940			0.10	20.87	7.76
	07:34	800	12	25 *	-	19.34	
		800	12	20% CaO	0.17	20.31	4.99
			10		0.22	19.31	15.64
				50% CaO	0.07	24.75	11.69
			30	20% CaO	0.09	23.80	23.03

*Mixture of make up with limestone and quicklime.

From a general point of view, the results obtained through Aspen PLUS software are not differing much from reality. Even existing some diversity of results, the margin of errors does not vary in a wide range [1-15%] being the average around 10% of relative error. While in points : 12.02.2015 at 04:04h and 03:44h the errors are in most time exceeding 10%, in other points : 11.02.2015 at 15:54h or 12.02.2015 at 00:34 the relative errors are barely exceeding 5%.

The solids fraction directed towards the calciner is usually very low. A significant increase on this value reach in some case high errors. (i.e. 13.2.2015 7:34h)

In the results can be observed that while limestone, just analyzed in one point highly affects the result of CO_2 concentration studied, quicklime barely influence this result. On the other side, the control of the fraction of solids going to the calciner also changes signficantly the final result of CO_2 concentration in the outlet gas of the calciner.

Regarding to molar conversion of the sorbent, in general the values obtained range between 8% and 15%. Later this range will be corroborate determining the molar conversion of some samples extracted from the carina plant.

One of the main important parameters –CO_2 concentration in the outlet gas from calciner- has been already studied but there are some other parameters which their comparison may is useful for a better knowledge of the model in Aspen PLUS.

The molar conversion is unknown in the data. The results obtained in Aspen Plus are the only one and can not be compared.

With regard to the combustor, the results obtained present huge differences with the data extracted from Carina Plant (data values). The results of the temperature in the combustor outlet are highly altered in comparison with reality. In major cases the relative error round the 40%. The main problem to face is that all necessary data for combustor is known, every parameter in it is fixed. Both the air inlet in the combustor and the propane mass are known values for each instant and also the pressure. The combustor temperature is function of these parameters so the cause for what results are extremely different is unknown. Following the same line, the CO_2 concentration in the combustor flue gas is also highly differing from the real value.

7 Thermogravimetric Analysis (TGA)

This chapter will use the sorbent that has been used in the Carina plant to analyze the effect of the temperature, time and CO_2 concentration in carbonation and calcination stage, thus subsequently obtaining results about the sorbent deactivation. These experiments will help to a better understanding in the decay of the sorbent activity, to know the intensity of this effect, see differences between samples and also to contribute to identify the optimum times for the carbonation operating and calcination operating conditions. There is a huge importance in the choice of an operating window for the calcium looping system because it affects on the CO_2 carrying capacity curves. Understanding the reaction and particle deactivation mechanisms is necessary to optimize process parameters to achieve high efficiencies.

The study is performed with a TGA apparatus. In this thermogravimetric analysis the sorbent is exposed under an environment of nitrogen and CO_2. The concentration of these two compounds will be varied along the study. The experiments are carried out at atmospheric pressure conditions.

Although the flue gas from coal power plants contains small amounts (ppm level) of SO_2, and these small amounts react with calcium sorbents, the influence of SO_2 cannot be analyzed in this work and neither its effect on the degree of CO_2 capture in the carbonate looping process.

Two different size particles of limestone sorbent have been used to perform the TGA tests: 100-300µm and 300-800µm.

7.1 TGA apparatus and operating method

The thermogravimetric analyzer (TGA) permits thermal studies changing physical and chemical properties of the material (here calcium sorbent) varying temperature over time. It has a high degree of precision regarding to mass change, temperature and temperature change. [63] The TGA records the weight change of a sample against temperature. It is a technique in which the mass of the sorbent is monitored as a function of temperature or time as the sample is subjected to a controlled temperature program in a controlled atmosphere. [64] In this work a Thermogravimetric analyzer (TGA) will be used to measure the sample reactivity along number of carbonation-calcination cycles.

TGA is commonly used to determined desired characteristics of materials that present either mass loss or gain due to decomposition, oxidation or loss of volatiles (such as moisture). Common applications of TGA are:

1) Materials characterization through analysis of characteristic decomposition patterns
2) Studies of degradation mechanisms and reaction kinetics
3) Determination of organic content in a sample
4) Determination of inorganic (e.g. ash) content in a sample.

The TGA apparatus used in this work is the TGA STA 449 F3 Jupiter.

The whole equipment of TGA consist on the TGA furnace, a heater/cooler, the bottles of flue gas and the program to monitor called Proteus Software.

The TGA apparatus consist of two sample crucibles that are supported by a precision balance. One of the crucible is empty and it is used as reference. The second crucible is the one containing the sample in each test. They both reside in the furnace and are subjected to the different established conditions in the program.

The program is used to set up the conditions under what the sample will be subjected. The temperature and sample weight are continuously recorded in it and a further analysis can be performed in the same program.

The desired gas mixture added into the furnace is supplied by a set of gas bottles via mass flow controllers. Three flows are entering the TGA apparatus. Two gas streams are supplied from the top, called purge 1 and purge 2, and the so-called protective flue gas is supplied by the bottom. The protective gas shrouds the balance mechanism from any heat or effluent gases; it is normally set a flow rate of 20ml/min and has been in all tests nitrogen. Both gases exit as one stream from the analyzer. In this work it is always going to be used two different gases: nitrogen and dioxide carbon.

One of the requirements of this mechanism it that before performing a test directly with the sample it is compulsory to perform a first correction test. The necessity of a base line correction will firstly show if there is some weird behavior under this conditions, or might something wrong is within the apparatus. Last, the correction test will be a reference for the test with the sample. The correction test takes into account just the crucible and the sample test the whole system (crucible + mass). With the correction test, an accurately result just over the sample can be obtained. After the test correction, the test with the sample can be carried out.

When what is pursued is to perform several tests under exactly the same temperature and concentrations conditions in the furnace but with different samples then is necessary just to perform one correction test and with this single correction test all other desired tests in the same conditions can be done with this one. This is the advantage of reproducibility. Reproducibility is the ability to create the same experiment over and over under exactly the same conditions. It is very important when comparing one set of data to another. And then any variation within the data will be due to a change in the sample and not due to an operator error.

7.2 Thermogravimetric analysis

As has been commented in previous chapters, the CO_2 carrying capacity is defined as the CaO molar conversion to $CaCO_3$ at the end of the fast carbonation stage of CaO in each carbonation-calcination cycle.

In the thermogravimetric analysis (TGA) the program shows different curves:

The temperature difference curve (DTA) shows the temperature difference between crucibles being so able to detect exothermic and endothermic changes.

TG curve measurements. This curve shows the weight of the sample in each instant. The carbonate content of the sample can be calculated from the weight loss during the sample phase change.

The conversion of CaO mol-% to $CaCO_3$ for each of the test can be calculated by assuming that the weight gained of the sample was due to the CO_2 reacting with CaO carbonation. The following equations can be used to calculate the CaO mol-% conversion during the carbonation and $CaCO_3$ mol-% during calcination:

$$CaO\ to\ CaCO_3\ conversion[mol-\%] = \frac{wt.gain\ during\ carbonation}{total\ wt\ loss\ during\ first\ calcination} \times 100 \qquad \text{Equation 7.1}$$

$$CaCO_3\ to\ CaO\ \ conversion[mol-\%] = \frac{wt.loss\ during\ calcination}{total\ wt\ loss\ during\ first\ calcination} \times 100 \qquad \text{Equation 7.2}$$

The following parameters are varied in the TGA test in order to see its influence: All varied parameters have been chosen according to several studies showing its influence [65].

-CO_2 carbonation concentration: 15% CO_2 – 10% CO_2

-Carbonation residence time: 10 min - 5 min

-Calcination temperature: 850ºC - 900ºC

-Recarbonation step*

In the following table are summarized the different tests performed:

Table: 9 Characteristics of the tests performed with TGA

	Carbonation		Calcination	Particle size	Others	Cycles
	CO_2 concentration	Residence time	Temperature			
Test1	15%	10min	900°C	100-300µm		22
Test2				300-800µm		22
Test3		5min				14
Test4	10%					18
Test5			850°C			12
Test6					Recarbonation stage*	5

*The recarbonation stage adds a new stage after carbonation with 85%CO_2 concentration from 650°C to 800°C and with a residence time of 3 minutes.

Test1 has been taken as a base and from this configuration one different parameter will be varied in each test. Test1 is subjected to a carbonation stage with 15%CO_2 at a temperature of 650°C and with a residence time of 10 minutes. In all TGA test carbonation temperature was kept unchanged at 650°C. The temperature of carbonation has been chosen according to the $CaCO_3$-CaO phase equilibrium data. The calcination stage will be subjected in all tests under the same CO_2 concentration of 30% –to achieve a more realistic situation- and with a residence time of 5 minutes.

The last test has been performed adding a recarbonation stage between carbonation and calcination stages. Recarbonation involves putting already carbonated particles in contact with high temperature and high CO_2 concentrations after the carbonation step. According to different studies summarized in M.Alonso [65] recarbonation might increases the residual CO_2 carrying capacity of the sorbent.

The results are displayed below.

The next graph represents weight loss of the sorbent over time of test1.

In a graphic in which concentration is represented over time, the slope of the curve represents the rate reaction. As can be observed in the following figure carbonation stage is divided in two phases. A fast reaction phase which is referred to the reaction reacting on the surface and a slow reaction phase produced by a reaction rate decreasing abruptly, that indicates the existence of a product layer and the transition to a diffusion limited regime.[10]

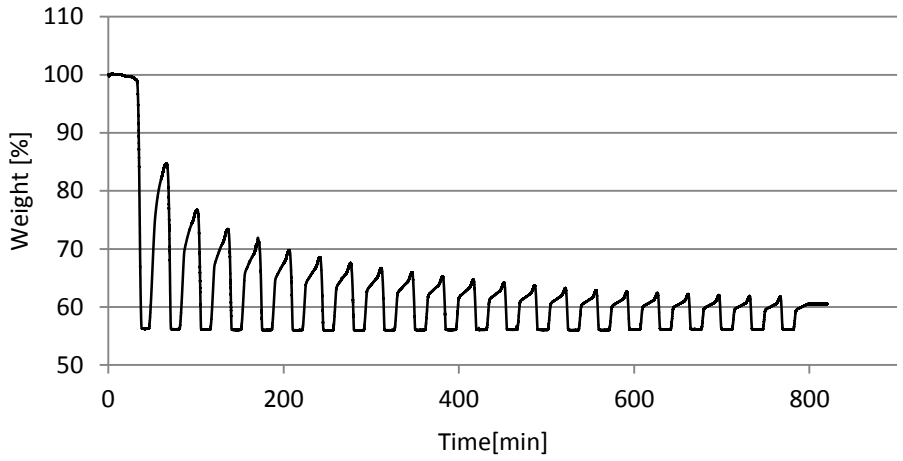

Figure: 59 Sorbent weight [%] over time [min] in test1.

In the next analyze is going to be compared the carrying capacity of the sorbent submitted to different conditions already mentioned. For this reason is important to clarify that the reaction curve is determined once the fast reaction rate is completed, from that instant CO_2 concentration has very small impact on conversion.

The comparison between the two first tests –test1 and test2- is aimed to see the influence of the particle sizes in the carrying capacity of the sorbent. As can be observed Figure: 60 presents slightly different results depending on the particle size of the sorbent. While the test1 – smaller particle size- tends to a value of 7.39% of sorbent carrying capacity after 100 cycles, the bigger size particles present a small increase enhancing the sorbent carrying capacity after 100 cycles tending to 9.61%.

The following graph depicts the carrying capacity of the sorbent in both situations in the first 20 cycles.

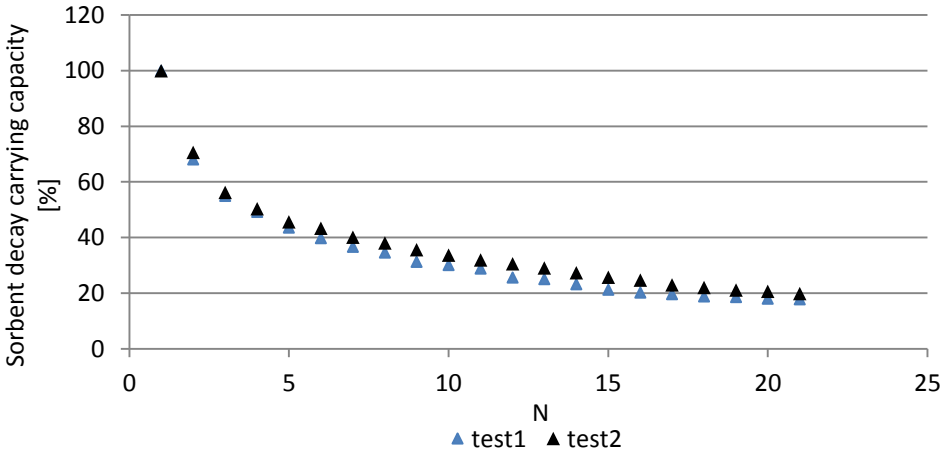

Figure: 60 Sorbent decay carrying capacity[%] over number of cycles [N] in test1,2.

From previous works was expected the particle size to strongly affect on the overall particle carbonation rates.

In this work a slightly difference is observed, resulting in an improvement of the carrying capacity of the sorbent with bigger particles size.

Nevertheless, according to [65]–a study which presents a review in all influencing parameters on the decay carrying capacity- settles that particle size has no influence on the deactivation curves.

In the following figure are depicted the results of carrying capacity of the sorbent in the remaining tests.

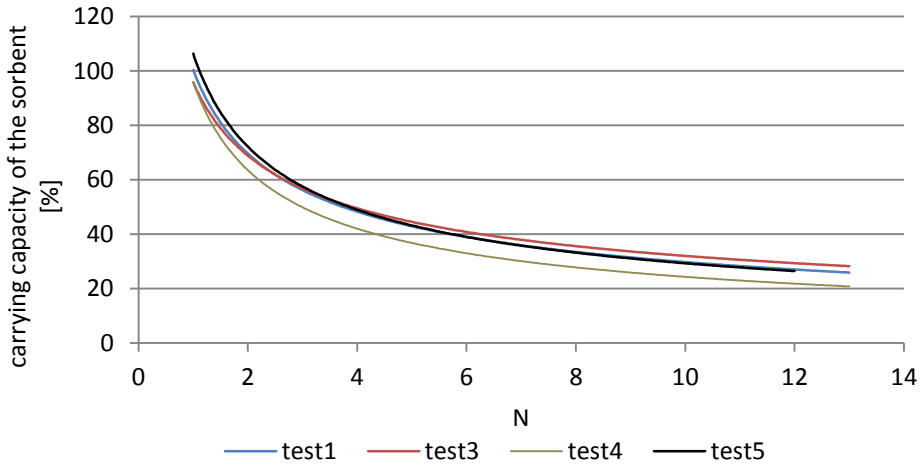

Figure: 61 Sorbent carrying capacity [%] over time [min] in tests1,3,4 and 5.

Test 3 -reduce the carbonation time to 5 minutes- presents the best results. Its carrying capacity after 100 cycles has been slightly improved from 7.39% from test 1 to 9.66%. According to [65] carbonation time has a negligible effect on decay conversion curves.

Contrary, the worst results are presented in test 4 -reduce to 10% the CO_2 concentration during carbonation stage- showing a tendency after 100 cycles of 5.83% compared with the 7.39% of carrying capacity of the sorbent in test1. The reaction rate is directly proportional to the difference between local and equilibrium CO_2 concentrations. When the local CO_2 concentration increases, remaining the equilibrium concentration the same because of the constant temperature of 650°C- the difference increase. This increase leads to a higher conversion.

By the other side, test 5 –referring to the temperature decrease in calcination stage- has not involved significant variation of the sorbent carrying capacity. The results of the carrying capacity of the sorbent in test 5 are slightly enhanced compared to test 1. Nevertheless according to a study recently performed [10] is affirmed that high temperature calcination accelerate the decay in carrying capacity.

Furthermore, test 5 presents an incomplete calcination in the earlier cycles. This might be produced because the lowering of the calcination temperature implies –keeping all other conditions in the same values –test1—

lower calcination time according to the equilibrium established by Barker 1962. The reason because incomplete calcination occurs only in the earlier cycles is due to in the earlier cycles is where more sorbent has to be calcined. As the particles follow a standard decay curve when submitted to carbonation calcination cycles, less sorbent is need to be calcined for what again complete calcination is achieved.

The following graph represents the previously commented.

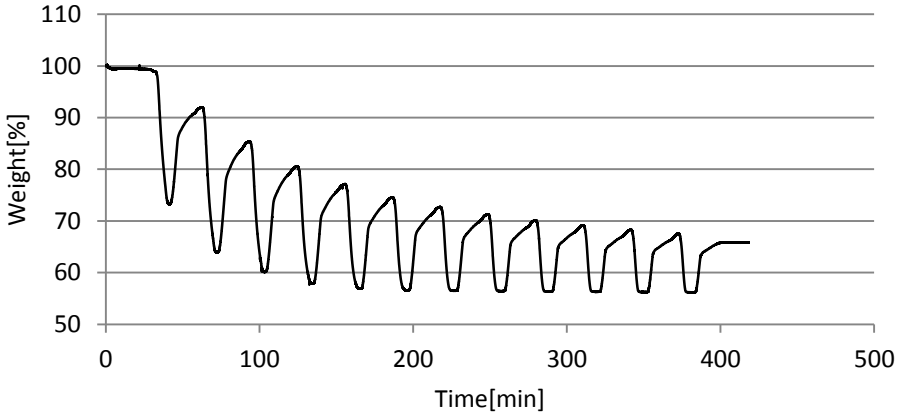

Figure: 62 Sorbent weight [%] over time [min] in test 5.

For this reason, it might be possible that when complete calcination in the earlier cycles had occurred, the carrying capacity would result higher, amply improving this value and matching with the study [10] recently performed corroborating that calcination temperature considerably affects the carrying capacity of the sorbent.

Recarbonation

Several researches to improve the activity of the sorbent are currently being carried out and the introduction of a recarbonation stage is one proposal to give with an effective solution.

According to M. Elena Diego [66] this enhancement can be achieved if recarbonation achieves high temperatures -750-800°C- and with high concentrated CO_2 atmospheres.

This could allow carbonate looping systems to operate with low limestone requirements. Furthermore this process can be easily integrated in the system without the necessity of any new reactant.

A recarbonation system is being integrated in la Pereda, Spain [67]

The results obtained in this work indicate that introducing an intermediate recarbonation stage mitigates the rate of conversion decay compare to ordinary carbonation-calcination cycles but in small extent. Figure: 63.

The enhanced carbonation conditions in the recarbonation appear to produce slightly higher formations of $CaCO_3$ what will generate more active CaO and increase the average CO_2 carrying capacity of the material. While the test1 tends to a sorbent carrying capacity value of 7.39% after 100 cycles, the adding of a recarbonation stage improves to a sorbent carrying capacity of 11.38% tendency after the same number of cycles.

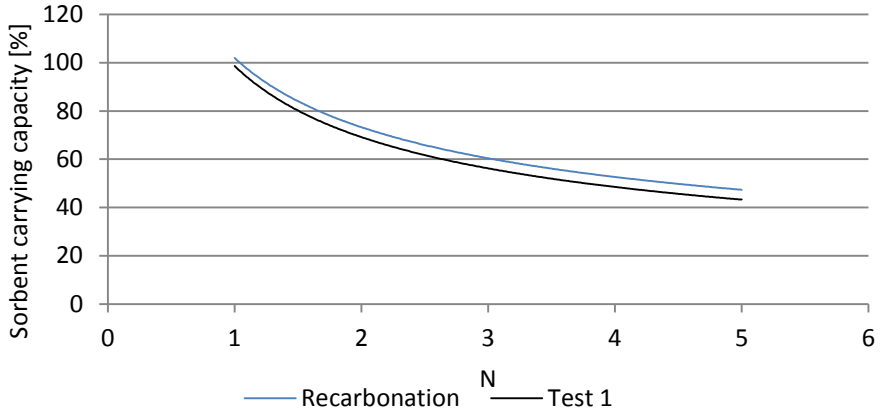

Figure: 63 Sorbent carrying capacity [%] over number of cycles [N] in test1,6

One cycle of the recarbonation test is shown in the figure below. There can be observed the evolution of $CaCO_3$ conversion in stage of carbonation and recarbonation. It can be seen that both conversion curves suffer a first fast reaction stage that is kinetically controlled until a certain conversion and a next slow period of reaction rate caused by diffusional resistances.

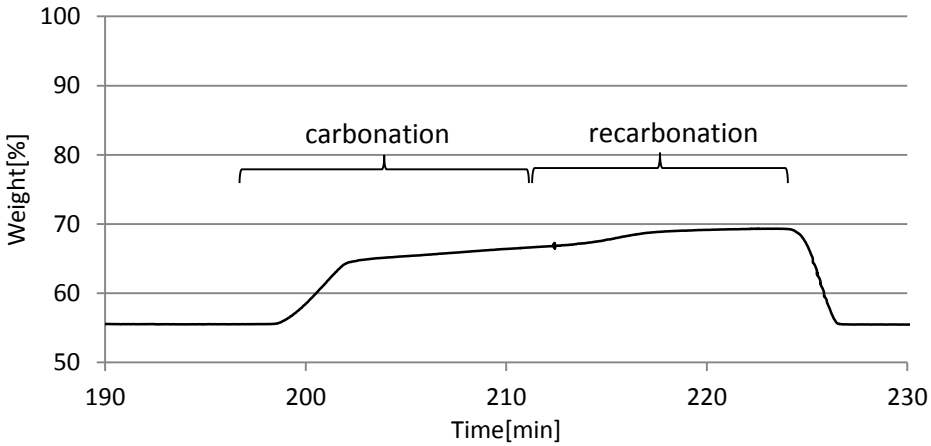

Figure: 64 Sorbent weight [%] over time[min] in one cycle carbonation/recarbonation/calcination

7.3 Solid Sample Analysis

Solid samples were collected from the Big bag, L-valve and Loop seal. All solids were removed from the system and weighed to perform a mass balance on the sorbent. The samples have been analyzed to define the conversion of the sorbent leaving the carbonator and it was carried out with the TGA previously presented.

The samples have been heated from ambient to 900°C at 25K/min in a nitrogen atmosphere resulting in complete calcination. Figure: 65 shows an example of the sorbent weight-loss curve when submitted under conditions of complete calcination.

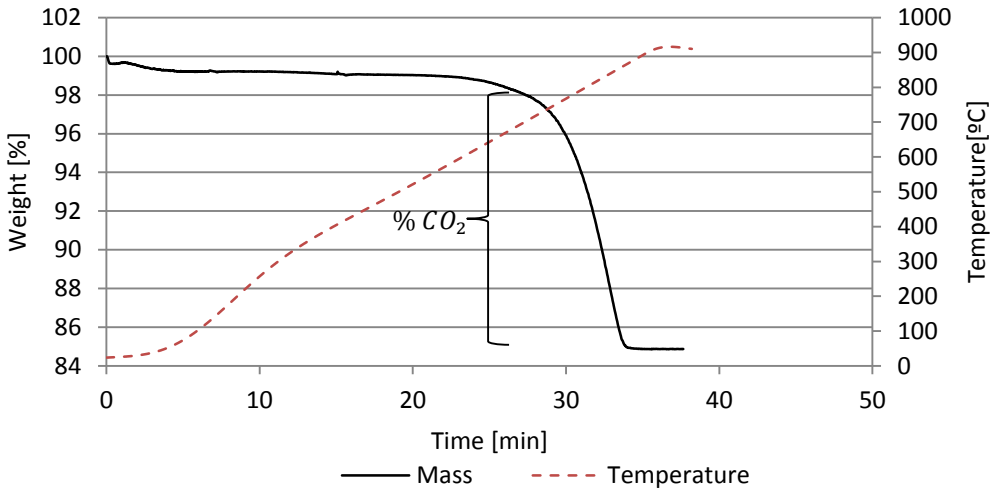

Figure: 65 Sample weight [%] over time [min] under fully calcination conditions.

To determine the sorbent conversion will be assumed that all loss in weight is because of the release of carbon dioxide from the calcination reaction. The carbonation conversion has been evaluated via equation7.3.

$$X_{carb} = \frac{m_{CaCO_3} - m_{CaO}}{m_{CaO}} \frac{M_{CaO}}{M_{CO_2}} \qquad \text{Equation 7.3}$$

Where m_{CaCO3} and m_{CaO} are the mass of calcium carbonate and calcium oxide respectively and *M* is the molar mass. The weight of the sample used to carry out the TGA test does not exceed 35mg.

Several samples where conducted under fully calcination to find out their carbonation conversion. The results obtained range between 6.9% and 20.7%. These values range between similar values than the values of carbonation conversion obtained through simulation with Aspen Plus in chapter 6.

8 Conclusion and outlook

An analysis of the influence of the main parameters in the system was carried out with the model according to the existing plant design. In addition a second model was implemented in order to determine the main emissions produced from coal combustion. The results were visually identified, discussed and assessed.
This allows a better understanding of the system.

A basic steady state Aspen PLUS model according to the existing pilot plant was successfully developed with proper results. Low errors were obtained from the simulations in comparison with the data extracted from test campaign in the 300kWtg pilot plant. An average error of 10% was reached with the simulations. The validation with experimental results demonstrate that the model calculates realistic results, reflecting a good development model and benchmarking despite the lack of some important variables that have been alleged by system resources.

The data obtained from test campaign in the 300kWth pilot plant was analyzed and described. Data were submitted as the inventory of solids and temperature of the reactor during the time plant operation. The results have given good CO_2 capture efficiencies often reaching 80%.
Regarding the evaluation of the sorbent performance by means of a TGA analysis; variables such as calcination temperature, carbonation time and the CO_2 concentration in this stage which can affect the deactivation of the sorbent were examined with samples from the latest test campaign. The particle size was also studied with a Thermogravimetric analyzer and the results were properly discussed.

In addition, an analysis subjecting samples of the test campaign under complete calcination was carried out to determine their conversion grade. Also values of molar conversions were obtained through simulation with Aspen Plus model using data from test campaign and similar values were obtained with the thermogravimetric analysis what indicates a good outcome and good reliability.

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